Vol. XXVIII. [OCTOBER, 1906.] No. 10.

THE JOURNAL

OF THE

American Chemical Society

SOME CONDITIONS INFLUENCING CONSTANCY OF VOLUME IN PORTLAND CEMENTS.

BY EDWARD DEMILLE CAMPBELL AND ALFRED H. WHITE.

Received July 21, 1906.

WHATEVER other faults an engineer may forgive in Portland cement, he demands that it shall be reliable and perform its duty for an indefinitely long number of years without deterioration. He dare not use a cement which may change its volume after it forms part of an important structure and thus cause the development of enormous internal strains. Instances of how powerful these strains may be, can be seen by any one thoughtful enough to observe the cement sidewalks over which he passes. The experiments here described form part of a series made with the view of studying the effect of changes in chemical composition upon the properties of finished cement, and especially upon that most important one of constancy of volume. The portion presented in this paper considers a range of composition quite common in American practice where the cement is not very highly limed and the percentages of alumina and iron oxide are together less than half the silica.

These cements have nearly all been under observation for five years, so that we feel warranted in presenting conclusions drawn from a study of their behavior during this period. The chief evidence is supplied by direct micrometric measurements of changes of volume undergone by bars of neat cement either lying in water at room temperature or kept in air at room temperature.

Such measurements were first carried out by Professor Bauschinger, of Munich, many years ago in an apparatus devised by him which bears his name. Measurements have since been made by others and have, in spite of some conflicting evidence, shown quite clearly that good cements expand somewhat in water and contract in air. These measurements have, however, been nearly all made by engineers upon commercial cements concerning which exact knowledge was lacking as to details of method of manufacture, temperature of burning, composition, and age since burning. The present experiments have so far as possible taken account of all these factors and it is believed present a more nearly quantitative estimate of their value than has hitherto been attempted.

Our measurements of change in volume have all been made upon bars of neat cement, and not upon mixtures of cement and sand or crushed stone, such as are used in practice. This added material, so far as constancy of volume is concerned, acts simply as a diluent for the cement. The change of volume due to the cement will vary with the percentage of cement and the relative area of empty spaces, which will depend upon the coarseness of the crushed stone used and the firmness with which the concrete is tamped into place. The use of bars of neat cement eliminates these large variables and allows a close comparison of results between the different kinds of cement. When applying these measurements of change of volume to concrete, it will be necessary to apply an arbitrary factor which will vary with every local condition, and cannot be considered here.

The behavior of Portland cement in concrete kept constantly or usually wet is entirely different from that which is kept dry, and demands separate treatment. The more complicated case of cement bars stored in water is first considered, and afterwards the relatively simple behavior of cement kept in air is treated.

After a brief consideration of the methods and apparatus employed, the paper divides itself into:

I. The influence of free lime and the effect of aging such cements.

II. The influence of free magnesia and the effect of aging such cements.

III. Some considerations determining the form in which lime and magnesia exist in cement including a preliminary study of the

probable equilibrium between free and combined lime, and free and combined magnesia in cements.

METHOD OF MANUFACTURING CEMENTS.

Where cements were to be burned in the laboratory each raw material was dried, thoroughly mixed and analyzed. The marls employed were ground to pass a 100-mesh sieve before using. All the cements described in this paper were made from a single clay which was not finely ground, but was disintegrated with water before mixing with the finely ground marl or other source of calcium carbonate. This method of disintegrating the clay left sand in suspension, and in calculating the proportion of basic material to be added, the assumption was made that silica in the form of quartz sand too coarse to pass a 100-mesh sieve was practically inert. The amount of coarse sand in the clay was determined and the necessary allowance made for it. Since one clay is used in all these experiments the results are strictly comparable with one another. The composition of the clinker as reported is calculated exclusive of this sand, which could average about $2^1/_2$ per cent. of the weight of the clinker.

TABLE I.—COMPOSITION OF RAW MATERIAL.

	No. 5 clay.	L. W. marl.	S. L. marl.	M. & W. marl.
SiO_2	46.91	1.21	0.90	1.36
Al_2O_3	15.89	0.25	0.20	0.55
Fe_2O_3	5.10	0.25	0.39	0.36
CaO	8.25	52.89	51.51	50.03
MgO	3.90	0.89	1.68	1.95

The raw materials were mixed with enough water to make a thin slurry, evaporated with frequent stirring to the proper consistency, moulded into cubes and burned in the laboratory rotary kiln as described in preceding papers from this laboratory.[1] Varying percentages of calcium sulphate in the form of plaster of Paris were added to the clinker, and the whole was ground till it practically all passed a 100-mesh sieve.

DESCRIPTION OF MICROMETER FOR MEASURING CHANGE OF VOLUME.

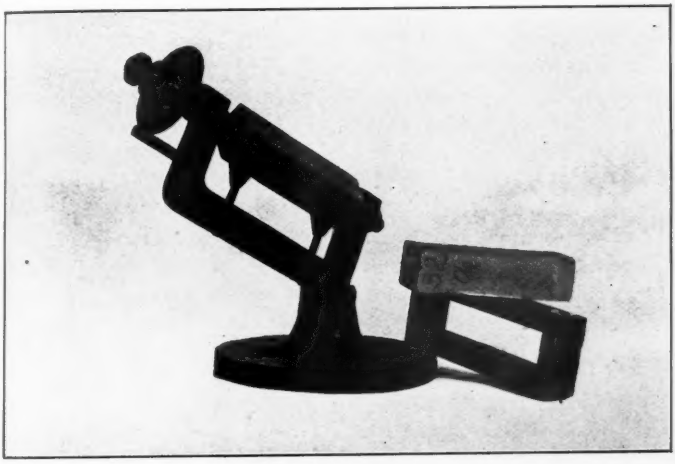
The change in volume was determined by measurement in a micrometer which possesses decided advantages in simplicity over the Bauschinger apparatus. As will be seen from the illustration, the rectangular bar is supported by two forks at an

[1] This Journal, **24**, 248, 969; **25**, 1103; **26**, 1142.

angle of about 45°, so that the bar rests by its own weight, with the embedded glass plate against the lower contact piece of the micrometer. The forks compel the bar to always take the same position when being measured, provided the same surface and the same end are placed upward each time. This arrangement always insures the same point of contact for the two ends of the micrometer and eliminates any error due to inequalities in the embedded glass plates. The upper part of the micrometer consists of a screw advancing 1 mm. at each revolution provided with a graduated disc of 50 mm. diameter divided into one hundred parts, each division thus being large enough to enable thousandths to be estimated. The final pressure exerted on the bar is controlled by a friction head turning on the spindle of the micrometer screw.

The expansion bars are made in a split mould 25 mm. square and 102.5 mm. long. Before putting the cement into the mould, a small glass plate is fastened by fine copper wire firmly against each end of the mould so it shall be in the center of the end of the cement bar. These glass plates are cut from microscope slides and are about 12 mm. square. All four edges of each plate are ground to a bevel of about 45° and it is placed in the mould with the small surface against the metal. This insures the firm embedding of the glass in the cement. When these glass plates have been carefully cleaned and thus wired to the ends of the mould, the latter is filled with the cement to be tested in the same way as a briquette mould, special care being taken to insure thorough bedding of the glass plates. After striking off smooth, the mould is allowed to stand in moist air, and when firm enough the experiment number is scratched in. After twenty-four hours in moist air in the constant temperature room, the fine wires holding the glass plates are cut close to the bar, and the bar removed and measured. The brass mould was made 102.5 mm. long because the ordinary microscope slides from which the glass plates are cut average 1.25 mm. in thickness so that the length of the prism of cement on which the expansion is measured is 100 mm. This enables millimeters of expansion to be read directly as percentages.

In making measurements care should be taken that the glass plates are carefully cleaned. The bar is then to be placed gently in the supporting forks, right side up, and allowed to slide gently



against the lower contact piece. It is not to be pressed against it by any force except its own weight. It is easy to insure the same position of the bar in all measurements by seeing that the inscription is always up and in position to be read by the observer. When taking observations, the bar is to be pressed very lightly against the forks with one finger of the left hand while with the other hand the micrometer screw is gently turned until the contact point rests against the upper glass plate. In order to insure firm contact at both ends of the bar the fixed head of the micrometer screw is turned after contact with a pressure about equal to that exerted in winding an ordinary watch. The micrometer is then unscrewed about a half-turn until well clear of the bar and is then screwed down again *slowly*, this time by means of the milled friction head. When contact has again been made, the friction head is carefully turned approximately a revolution, so that the pressure on the expansion bar shall be that due to the friction of the movable head only. The reading of the micrometer is then taken, the head unscrewed until free, the bar loosened and the process repeated. Usually four or five such readings are made on each bar. The maximum variation in a series of five such observations will not exceed 0.003 mm. and is usually not over 0.002 mm. Different observers without more than a few minutes' initiatory practice will duplicate each other's readings within these same limits.

It is best to keep the bars, whether in water or air, together with the micrometer in a room of fairly constant temperature. The temperature coefficients of expansion of iron and cement are so close together that provided the bars and micrometer are at the same temperature, variations of a few degrees in the temperature of the room will not appreciably affect the measurements.

INFLUENCE OF FREE LIME.

Free lime has always been recognized as injurious in Portland cements, but it has been difficult to study its quantitative influence, because of the impossibility of determining by analysis how much of the lime in a clinker is free and how much is combined. It was decided to make a cement of otherwise normal composition which should contain a known amount of free lime. In order to provide a standard with which to compare such a cement, a normal mixture was prepared and burned as Expt. 77.

To a duplicate raw mixture was added calcite in grains coarse enough to remain as free lime in the cement (Expts. 78 and 81). These cements were made from L. W. marl and No. 5 clay whose composition has been given in Table I. The normal cement, 77, had the following percentage and molecular composition:

EXPERIMENT 77.

	Percentage.	Molecules.
SiO_2	24.52	100.
Al_2O_3	8.13	19.6
Fe_2O_3	2.79	4.3
CaO	61.66	270.7
MgO	2.89	17.7

This was burned in the rotary kiln at 1522°, which was as high a temperature as could be carried without causing the clinkers to stick together. The clinker was black, hard and brittle. A portion ground when fresh required 2.5 per cent. plaster of Paris to delay the initial set enough to work. With this amount, the initial set was ten minutes and final set twenty minutes. A pat twenty-four hours in air and twenty-four hours in boiling water remained perfect and hard. Bars 77 A and 77 B were made at that time. Another portion of clinker stored in the laboratory for forty days was ground with 1.5 per cent. plaster of Paris and took its initial set in three minutes and final in fifteen minutes. The pat test as before was perfect. The remainder of the cement with 1.5 per cent plaster of Paris was then stored, ground, an additional six months. Its initial set after that period was eight minutes and final two hours. Expansion bars 77 C and 77 D were made at that time. The further discussion of the behavior of this cement is found in connection with the following experiments. It only need be noted that, as was intended, it proved to be in every way a good cement.

The cements to show the influence of free lime (Expts. 78 and 81) were made from a raw mixture, a duplicate of Expt. 77, to which was added a weighed amount of pure calcite crushed and sized to pass a twelve-, but be retained on a twenty-mesh sieve. This relatively coarse calcite was mixed with the normal slurry which was moulded into cubes, dried and burned in the usual manner. It is fairly certain that such coarse calcite would remain almost wholly as free lime in the clinker. The mixture was burned at 1483°, a temperature a little below the average,

but yielding a strong and apparently well-burned clinker. Assuming that all the lime from the crushed calcite remained in the free state, the clinker would contain 2.80 per cent. of free lime, and have the following percentage and molecular composition.

EXPERIMENTS 78 AND 81.

	Percentage.	Molecules.
SiO_2	23.83	100.
Al_2O_3	7.91	19.6
Fe_2O_3	2.72	4.3
Combined CaO	59.93	270.7
Free CaO	2.80	12.6
MgO	2.81	17.7

A portion of this clinker ground with 1.5 per cent. plaster of Paris required 23 per cent. of water for normal consistency and took its initial set in two hours and forty-five minutes. The final set was slow, but not exactly noted. A pat after twenty-four hours in air and twenty-four hours in boiling water was warped loose from the glass and very weak. Neat briquettes made at that time, kept in water and broken after seven days, twenty-eight days and six months showed, respectively, tensile strengths of 295, 630 and 862 pounds per square inch. Two expansion bars were made at this same time, 78 A to be kept in water and 78 B in air. The data of measurements are given in Tables II and IV at the close of the paper and the discussion is given below in connection with the following experiment. The other portion of clinker remaining unground was exposed outdoors in an open box during the month of June and after one month's exposure, was ground with 1.5 per cent. plaster of Paris as before. The cement then took 25 per cent. of water for normal consistency and gave an initial set of three minutes and a final set of five. After twenty-four hours in air and twenty-four hours in boiling water the pat was loose from the glass, slightly warped but very strong.

This cement then was manifestly unsound when fresh, as was to have been expected from the free lime, but behaved much better under the boiling test after the clinker had been stored exposed to the weather for one month. The unexpected fact shown is that this cement containing free lime was slow-setting when fresh, but after one month's storing became so quick-setting as to be useless. It is also to be noted that in spite of its free lime, the tensile tests up to six months were good.

It was deemed best to duplicate this experiment and Expt. 81 was accordingly made as an exact duplicate of Expt. 78, except that the temperature of burning was slightly higher, 1502° as compared with 1483° of the previous experiment. It being desired to determine the length of time required to completely hydrate free lime existing in clinker if the clinker was exposed freely to the weather, the main body of the clinker was thus exposed during the summer and samples were taken at the end of each month and tested for soundness by the boiling test. The data of the pat tests are on the next page.

This experiment confirms Expt. 78 in showing a relatively slow set on the fresh cement changing to an extremely quick set on exposure of the clinker to the weather for a few weeks. As would be expected, the presence of free lime caused nearly complete disintegration of the pat made from fresh cement. The progressive improvement in the behavior of the pats on boiling, rising to a perfect pat at the end of three months showed that by this time the free lime had probably become completely hydrated. The cement was still very quick-setting (see No. 4). On further exposure of the clinker to weather for a total of ten months, the pat still remained perfect but the cement with the same amount of gypsum added had become slow-setting, requiring nearly four hours for initial set (see No. 8). Storing the ground cement in the laboratory for the same period had a slight effect in the same direction (see No. 7). The conclusion is therefore reached that the bad effects of free lime may be eliminated by aging the clinker exposed to the weather, or the ground cement under cover. The cement may become very quick-setting during this process, but will probably get slower again, if sufficient time is allowed.

BENEFICIAL EFFECT OF AGING CEMENTS CONTAINING FREE LIME.

The beneficial effect of aging these cements has been in part brought out by the preceding study of the boiling tests, but it may be best studied quantitatively from the measurements of the expansion bars kept in water whose data are given in Table II, p. 1300, and discussed here, and from the measurements of bars kept in air which will be discussed under a separate heading further on in the paper.

The influence of free lime in cements used fresh and kept under water is best observed by comparing bar 78 A containing free

Treatment of cement.	Plaster of Paris added.	Water. Per cent.	Corresponding expansion bars.	Initial set.	Final set.	Result of pat test 24 hrs. in air and 24 hrs. in boiling water.
1. Fresh	1.5	23	Expt. 78, A and B.	45 min.(?)	1 hr.	Warped away from glass, badly cracked and easily rubbed to sand.
2. Clinker 1 mo. to weather	1.5	23		Less than 15 min.		Warped loose from glass and checked.
3. Clinker 2 mos. to weather	1.5	24		Less than 4 min.		Loose from glass but very strong.
4. Clinker 3 mos. to weather	1.5	24		Within 1 min.		
	2.0	24	Expt. 81, A and B.	?	?	Pat perfect.
5. Clinker 4 mos. to weather	2.0	23				Pat perfect.
6. Clinker 4 mos. to weather. Ground 4 weeks in lab.	2.0	23	Expt. 81, C and D.	5 min.	15 min.	Pat perfect.
7. Clinker 4 mos. to weather. Ground 6 mos. in lab.	2.0	23	Expt. 81, E and F.	7 min.	30 min.	Pat perfect.
8. Clinker 10 mos. to weather	2.0	22	Expt. 81, G and H.	3 hrs. 45 min.	5 hrs. 30 min.	Pat perfect.

lime with the similar but normal 77 A. Bar 77 A, which has been immersed in water for five years, showed the gradual expansion usual with good cement and the slight drop in the curve at about six months which is also customary. The corresponding bar 78 A showed the effect of its free lime by an abnormal expansion during the first seven days. During this first week it expanded 0.220 per cent. which is more than the corresponding 77 A showed in five years. It continued to expand at a comparatively rapid but diminishing rate until after two months the rate of expansion had settled down to practically a normal rate, showing that the free lime had become completely hydrated by two months' immersion in water. The later history of the bar shows nothing abnormal, although its high expansion in its early history brings its total after five years to 0.451 per cent.

The effect of aging these cements before use is shown by bars 77 D and 81 B, C, E and G. Bar 77 D was made from the normal cement containing no free lime which had been ground with 1.5 per cent. plaster of Paris and then stored in the laboratory six months. The beneficial effect of aging even a normal cement is shown by its much greater constancy of volume as compared with the fresh cement. At the end of two months its expansion was only one-fifth as much as the fresh cement, and its last measurement showed a total expansion, after four years in water, of only 0.052 per cent. This cement also shows the customary slight contraction in volume after three months which in this case brings its volume slightly less than it was initially. This cement, 77, then, behaves throughout as a well-made cement should.

The similar cement, 78, containing 2.8 per cent. free lime showed abnormal expansion when worked up fresh. Expt. 81, which was a duplicate of 78, was purposely not worked up fresh, but was stored as clinker exposed to the weather for four months.

A portion of it was then ground with 2 per cent. plaster of Paris and an expansion bar was made (81 B) which placed in water showed no more expansion than a normal cement which had aged the same length of time. Another bar (81 G), made from a clinker exposed to the weather ten months, showed little difference in its behavior from a normal cement which had been aged. These bars with the corresponding pat tests indicate that the influence of free lime disappears completely if the clinker is stored open to the weather for four months prior to grinding, and that such

cements will be more constant in volume than will most cements of proper composition but worked up fresh.

THE INFLUENCE OF FREE MAGNESIA ON PORTLAND CEMENT.

It was recognized over twenty years ago that magnesia might be a harmful constituent of cement. In 1888 the German Association of Portland Cement Manufacturers appointed a commission with R. Dyckerhoff as chairman to thoroughly investigate the question. This commission after a series of experiments lasting over five years reported in 1895[1] that they could not agree upon a unanimous report. Dyckerhoff maintained as the result of observations upon cements made by him that more than 4 per cent. of magnesia could not safely be allowed in Portland cement. The majority of the committee dissented from this opinion and cited instances of cements with much higher magnesia content which had stood severe tests and had been under observation for years enough to have developed any defects which might have been latent in them. They maintained that magnesia exerted no ill-effect provided the magnesia was calculated as replacing an equivalent amount of lime in the percentage formula

$$\frac{CaO}{SiO_2+Al_2O_3+Fe_2O_3}=1.8\text{–}2.2.$$

The conclusions of the majority of the committee were apparently based not on cements which they had themselves manufactured, but on the analysis of commercial cements high in magnesia which had proved themselves safe.

Four years later other experiments were reported by Oskar von Blaese,[2] who manufactured cements containing varying percentages of magnesia. The raw materials were finely ground and burned in a fixed kiln, and the cements showed throughout a very great constancy of volume. The cements with higher percentages of magnesia showed abnormal expansion, but the conclusion of the author is that 5 per cent. of magnesia is entirely allowable in cements. Further evidence of the influence of magnesia was brought forward by Grauer,[3] who presented in 1902 results of five-year observations on the changes in volume of a number of cements containing magnesia up to 4 per cent. He found that

[1] Thonindustrie Ztg. 19, 473.
[2] Ibid. 23, 214.
[3] Ibid. 26, II, 1031.

magnesia up to this amount exerted no marked harmful influence. Unfortunately, he made no experiments with cements containing over 4 per cent. magnesia.

It is curious that none of these investigators seem to have paid any attention to the possibility that the erratic behavior of magnesia was due to the form in which it existed in the cement. Free lime in cement has always been recognized as dangerous, but, when in proper combination with silica and alumina, it forms the principal constituent of cement. It seemed to us there was a possibility that magnesia, like lime, was harmful only in the free state, and that it might sometimes be in entirely harmless combination.

The first step in investigating this question was to determine whether magnesia could be made to combine with silica and alumina as lime does; in other words to make an all-magnesia cement. This successfully accomplished, the next step was to determine quantitatively the effect of magnesia existing undoubtedly in the free state. The problem then was to apply the knowledge thus gained to the solution of the difficult question of determining the equilibrium between free and combined lime, and free and combined magnesia. It is not claimed that anything more than a successful beginning has been made on this problem of equilibrium, but some light has been thrown upon it.

PREPARATION AND PROPERTIES OF AN "ALL-MAGNESIA" CEMENT.

Expt. 80 was made to determine whether magnesia could possibly completely take the place of lime and produce a hydraulic cement which did not show abnormal expansion. The raw materials used were No. 5 clay (for composition see Table I), and chemically pure hydrated magnesium carbonate containing 36 per cent. MgO. These were so proportioned as to give a clinker of the following percentage composition and molecular ratio. The cement necessarily shows a small amount of lime coming from the clay used.

EXPERIMENTS 80 AND 82.

	Percentage.	Molecules.
SiO_2	28.91	100.
Al_2O_3	9.79	20.0
Fe_2O_3	3.14	4.1
CaO	5.08	18.9
MgO	53.07	274.7
	99.99	

This was burned at 1496°. The clinker was apparently well burned, strong and of good appearance. It was ground with 1.5 per cent. of plaster of Paris. A pat required 21 percent. of water for normal consistency, took initial set in fifty-two minutes and final set in nine hours. After twenty-four hours in air and twenty-four hours in boiling water, the pat was perfect in appearance and firmly adherent to the glass, but if broken loose was weak as compared with good Portland cement and could be easily rubbed to sand between the fingers. Neat briquettes made from this cement and kept in water gave a tensile test of 27 pounds per square inch after seven days and 43 after twenty-eight days with a continuous gain to 162 pounds after two years. The difference shown by these tests between this cement and a regular Portland is one of degree only. A bar made from fresh cement and kept in water showed an expansion somewhat *less* than is normal for fresh Portland cement. The measurements extend for five years and are given in Table II.

A duplicate of this experiment was made as Expt. 82, the only difference being that the temperature of burning was somewhat higher—1538°. The clinker resembled that from the other experiment. A portion of the clinker was ground fresh with 1.5 per cent. plaster of Paris as in the previous experiment, required 23 per cent. of water instead of 21 for normal consistency, and set somewhat more rapidly, the initial set being twenty minutes and the final five hours. After subjecting to the boiling test the pat was perfect and stronger than in Expt. 80. After the clinker had lain in the laboratory for two weeks, another sample was ground and a pat was made. The initial set had become retarded in that time to one hour and thirty minutes and the final set to seven hours. After the remainder of the clinker had been stored in the laboratory four months, another sample was ground and an expansion bar made. This bar has been kept in water and under observation for four years, the full table of measurements being in Table II. The expansion at the end of four years is only 0.080 per cent., as compared with 0.100 per cent. on the duplicate experiment, 80, which was burned at a somewhat lower temperature and worked up fresh.

These experiments clearly show that it is possible to make a hydraulic cement whose molecular ratio $RO:RO_2+R_2O_3$ is practically that of many commercial Portland cements but in

which the lime is almost entirely replaced by magnesia. This cement clinkers at a temperature about that for normal Portland and yields a cement which, except for its inferiority in ultimate strength, meets all the tests demanded of Portland. In fact five-year measurements in water show it to be superior to most cements in constancy of volume.

EFFECT OF ADDED FREE MAGNESIA AND COMBINED MAGNESIA.

The next step was to make a series of comparative tests to determine the effect of adding known amounts of free magnesia and combined magnesia to a finished cement. For this purpose fresh cement clinker was procured from one of our older Michigan mills. This clinker had been put through the ball mill so that most of it would pass a twenty-mesh sieve, but no gypsum had been added to it. It had the following composition:

EXPERIMENTS 83 AND 85.

	Percentage.	Molecules.
SiO_2	24.54	100.
Al_2O_3	6.80	16.4
Fe_2O_3	3.17	4.9
CaO	63.10	276.9
MgO	1.87	11.4

Portions of this crushed clinker were ground with the addition of 1.5 per cent. plaster of Paris, and varying proportions of free magnesium oxide and of crushed magnesian cement from Expt. 82 were added to it. The free magnesia was obtained by burning in the rotary cement kiln chemically pure magnesium carbonate at a temperature of not less than 1500°. The entire set of nine bars was worked up within two weeks. 83 A is cement ground without any addition save plaster of Paris. To B, C, D and E were added, besides, 1, 2, 3 and 4 per cent. respectively of hard-burned free magnesia while to F, G, H and I were added 2, 4, 6 and 8 per cent. of the magnesian cement, Expt. 82, approximately equivalent to 1, 2, 3 and 4 per cent. of combined magnesia. Tensile tests made on ten neat briquettes of each series extending over a period of three years did not indicate that the presence of free magnesia lowered the ultimate strength. Pat tests of the cements containing added magnesia after twenty-four hours in boiling water showed no signs of cracking or warping although occasionally and irrespective of the magnesia content, they were loose from the glass. The test of twenty-four hours in boiling

water is therefore not to be relied on to indicate free magnesia even when present to the extent of 4 per cent.

The data of measurements in the nine bars of this series kept in water up to five years are given in Table III. Examination of the figures shows that the original cement (bar 83 A) showed, during the first three months, a relatively rapid expansion which seems to be characteristic of all fresh cements. During the next month it contracted slightly and slowly expanded again until at the end of a year it had reached the same volume as at three months. This drop in the expansion curve seems to be characteristic of all fresh cement and is probably associated with the usual decrease in ultimate strength of neat briquettes in a corresponding period. From one year to five years the expansion proceeded slowly but continuously. This bar, as well as the others described in this paper, will be kept under further observation.

Bars 83 F, G, H and I, containing 1 to 4 per cent. added *combined* magnesia, show the same general expansion as the original cement, but instead of causing a greater expansion this added combined magnesia has *diminished* the expansion slightly, probably because the added magnesian cement itself undergoes such slight changes in volume. After five years these four bars average 0.134 per cent. expansion while the original commercial cement showed 0.144 per cent.

Bars 83 B, C, D and E, on the other hand containing 1 to 4 per cent. of added *free* magnesia, show the same drop in the curve after three months that the others do, and up to this time there is nothing to indicate the presence of free magnesia. After one year, however, free magnesia to the extent of 2 per cent. or more begins to cause evident expansion, and its effect becomes progressively greater as time elapses, until at the end of five years we note that bar 83 E with 4 per cent. of free magnesia has expanded over 1 per cent. The bar at the end of this period is apparently strong and sound and will be observed further. Summarizing the results at the end of five years, we find the following percentages of expansion:

Original cement..... 0.144

MgO added. Per cent.	A in free state. Per cent.	B combined. Per cent.
1	0.146	0.130
2	0.203	0.130
3	0.382	0.138
4	1.010	0.135

The above figures demonstrate conclusively that magnesia combined in the form of Expt. 82 does not cause expansion and show that the influence of free magnesia up to 1 per cent. is very slight. The dangers attending the presence of this constituent in larger amounts are forcibly shown by the above figures, but the insidious and slow development of the evil effects of free magnesia require further emphasis. Even cement 83 E with its 4 per cent. of free magnesia would have passed perfectly any standard physical tests, and yet after five years in cold water it has expanded over 1 per cent. and there is no indication that the end is reached. Indeed the expansion during the last year is nearly as much as the total of the preceding four years.

EFFECT OF AGING CEMENT CONTAINING FREE MAGNESIA.

After the bars for Expt. 83 were made, a certain amount of the ground mixtures was left. In order to confirm the results of Expt. 83 and also to observe the effect of aging the ground cement, a similar set of bars known as Expt. 85 was made from this surplus material. It was worked up after being kept in a basement cupboard for six months in bottles two-thirds of the time stoppered and the last two months with the stoppers removed. Bars 85 C and D form an addition to the series, being made from the crushed clinker stored a similar length of time in a cupboard but freely open to the air all the time. In all, nineteen bars were made in this series, ten being kept in water and nine in air. Four-year measurements of bars kept in water are given in Table III, while those stored in air are in Table IV.

A study of these figures on the bars of Expt. 85 in water shows that the first expansion, after seven days, averages less than two-thirds as much as in the cement not aged. The next point to be noted is that the contraction in volume observed in fresh cements after about three months is almost eliminated in this aged cement. The change in volume except for one or two slight exceptions is steadily an expansion, but after one year the measurements are still notably below the corresponding fresh cements. The last measurements are after four years with the following results as compared with the fresh cement at a corresponding period.

EXPERIMENTS 83 AND 85.

	Fresh cement. Per cent.	Aged cement. Per cent.
Original cement.....	0.139	0.105
1 Per cent. free MgO added.....	0.144	0.150
2 " " " " "	0.190	0.165
3 " " " " "	0.253	0.240
4 " " " " "	0.562	0.615
1 " " combined MgO added...	0.129	0.115
2 " " " " " ...	0.124	0.107
3 " " " " " ...	0.130	0.099
4 " " " " " ...	0.130	0.084

The original cement aged six months after grinding and before using shows only 75 per cent. of the expansion of the cement worked up while fresh. The bars to which the magnesian cement was added show similar decreased expansion and the difference in favor of the aged cement is greatest in the cases of the bars with largest additions of the non-expansive magnesia cement. The bars with added free magnesia have, on the other hand, expanded practically as much as the fresh cement.

The net result of this experiment is to confirm the harmful and slowly appearing effect of free hard-burned magnesia in cement. Aging the cement before using retards the expansion for a year or two, but the relief is only temporary for after four years the expansion due to free magnesia is about as bad in the aged as in the fresh cement. The conclusion is therefore reached that aging will not prevent the evil effects due to free magnesia, although it may delay their appearance for a year. This is in contrast to the effect of aging cements containing free lime where the harmful effects of free lime may be completely removed by aging. The failure of the aging process to afford relief from magnesia is undoubtedly due to the extremely slow rate of hydration of this substance, which does not seem to hydrate in air at any measurable rate.

COARSENESS OF RAW MATERIALS AS A FACTOR CAUSING FREE LIME.

Under the heading "Influence of Free Lime," we have already discussed Expts. 78 and 81 to which such coarse particles of calcite were added that most of it was certain to remain as free lime in the finished cement. The effect of smaller differences in fineness, such as exist in marls from different sources, is shown by Expts. 74, 75 and 79. The L. W. marl used in Expt. 79 (and also in Expts. 77 and 78) was exceptionally uniform and

almost impalpably finely precipitated calcium carbonate. The S. L. marl of Expt. 74 consisted largely of shells. It was ground to pass a 100-mesh sieve but the particles then were much coarser than those of L. W. marl. The M. and W. marl (Expt. 75) was intermediate between the two in fineness.

The effect of these differences in the physical properties of the marl is shown in Expts. 74, 75 and 79 where the three marls are combined with the same clay. Expts. 74 and 79 have nearly the same molecular formulas and are burned at practically identical temperatures. Yet 74 with coarser marl clearly shows free lime while 79 is sound. This is shown not only by the boiling tests but by the expansion bars. Bar 79 A from fresh cement showed after seven days in water an expansion of only 0.025 per cent. and cannot have contained a trace of free lime, while bar 74 A made from cement which had the advantage of being stored in the laboratory seven weeks after grinding and before being made up, showed after seven days in water an expansion of 0.190 per cent., nearly eight times as high as 79 A and only to be explained by the presence of free lime. Bar 74 D, made from the same cement stored as ground cement in the laboratory for seven and a half months, showed only normal expansion and confirmed the results previously observed in Expt. 81, that the effect of free lime completely disappears on sufficient aging.

Expt. 75 (medium grade marl) also shows considerable free lime, as is evidenced by the seven-day measurement on bar 75 A in water with its expansion of 0.200 per cent. The effect of aging in eliminating free lime is similarly shown in bar 75 D where the expansion on the seven-day measurement is reduced to 0.020 per cent. by storing the ground cement seven months.

The chemical compositions and molecular ratios of the cements 74, 75, 77 and 79 are given in the subjoined table.

	Percentage composition.				Molecular composition.			
	74.	75.	79.	77.	74.	75.	79.	77.
SiO_2	22.90	22.50	23.43	24.52	100.	100.	100.	100.
Al_2O_3	7.64	7.72	7.77	8.13	19.7	20.3	19.6	19.6
Fe_2O_3	2.81	2.70	2.67	2.79	4.6	4.5	4.3	4.3
CaO	59.59	62.99	58.92	61.66	280.2	301.5	270.7	270.7
MgO	7.05	4.06	7.21	2.89	46.7	26.9	46.0	17.7
CaO + MgO	.....	.....	.....	.....	326.9	328.4	316.7	288.4

It will be noted that the CaO molecular ratio increases in the order 79, 74, 75, but the difference between 79 and 74 is too small

to account for the decided showing of free lime in 74 while it is absent from 79. The difference must be due to the coarser marl of 74. Neither should the free lime in 75 be ascribed to its somewhat higher lime ratio, for Expt. 105 from finely ground material reported in a previous paper gave a perfectly sound cement when burned at 1475° with higher RO ratio of 315.2 molecules of lime and 19.1 magnesia to 100 of silica. This same mixture, No. 105, before its very intimate grinding failed to give a sound cement even when burned at a temperature above 1600°. The details of this experiment showing influence of fineness of grinding on the clinkering process form the subject of a separate paper already published by one of us.[1]

These experiments emphasize the fact, which most mills now realize, that extremely fine grinding of raw materials is necessary to insure the production of cement which shall be sound, even when fresh.

FREE MAGNESIA CAUSED BY COARSENESS OF RAW MATERIALS.

There are five cements available for this discussion. The same lot of clay was used for all of them, but the basic constituents were from various sources, as stated below. The details regarding the manufacture of all of these cements have been given in the preceding portions of this paper. The data most important for this discussion are repeated here.

Expt. 80 and 82. "All-magnesia" cements. Very finely divided. Chemically pure magnesium carbonate used.

Expt. 77. Finely divided L. W. marl.

Expt. 79. Finely divided L. W. marl and finely divided magnesium carbonate.

Expt. 74. Coarser S. L. marl and finely divided magnesium carbonate.

Expt. 75. Moderately fine M. and W. marl.

Expt. No.	MgO. Per cent.	Molecules to 100 of SiO_2. MgO.	CaO.	CaO and MgO.	Temp. of burning.	Estimated free MgO. Per cent.
77.....	2.89	17.7	270.4	288.4	1522°	none
75.....	4.06	26.9	301.5	328.4	1482	2–3
74.....	7.05	46.7	280.2	326.9	1521	3+
79.....	7.21	46.0	270.7	316.7	1474	2–3
80.....	53.07	274.7	18.9	293.6	1496	none

Of these cements only the first in the table, Expt. 77, has a

[1] This Journal, **25**, 1103.

low enough percentage of magnesia to pass the most rigid specifications. As has been shown already, the slight expansion of this cement when kept in water for five years assures us that it contains no measurable amount of free magnesia. The next cement in order (Expt. 75 with 4.06 per cent. MgO) has low enough magnesia to satisfy many of the specifications. It is, however, made from a coarser marl and is burned at a temperature which is not extraordinarily high, although it should have produced sound cement from an intimately ground raw mixture. The cement contains free lime, as previously noted. A portion of this cement was stored after grinding long enough to destroy the effect of free lime, and then worked up as bar 75 D, which was put in water and has now been under observation for four years. Its low initial expansion shows that the effect of the free lime has disappeared in the aging process, but its expansion at the end of four years reaches the figure of 0.177 per cent., far too high for a sound aged cement. It may fairly be compared with bar 77 D made from sound cement which had been aged about the same time, whose expansion in the same period was only 0.052 per cent., only one-third as much as the cement under consideration.

This tripled expansion of 75 D as compared with 77 D must, so far as we can see, be attributed to the presence of free magnesia. The amount of this free magnesia may be approximately estimated by comparing it with the measurements on Expt. 85 already reported, where varying amounts of free hard-burned magnesia were added to a sound cement which was then aged similarly to Expt. 75. By comparison with the bars of Expt. 85 we estimate that this cement, 75, contains between 2 and 3 per cent. of free magnesia. The reason for this free magnesia is probably to be sought in the relative coarseness of the raw material, which also prevented all the lime from combining. With finely ground raw materials, cement of this composition and burned at this temperature should show much better combination than this one does.

The third cement in the list, Expt. 74, with 7.05 per cent. magnesia, shows an expansion of the bar 74 D of similarly aged cement, amounting to 0.245 per cent. at the end of four years. In comparison again with bar 77 D the increase of 0.193 per cent. over 77 is attributable in the same way to free magnesia. Again estimating by comparison with Expt. 85, the amount of free magnesia required to give an expansion of 0.245 per cent., we

arrive at the probable amount of free magnesia in this cement as a little over 3 per cent. This was burned at as high a temperature as is usual in practice but was made from shell marl as before noted and therefore contained both free lime and free magnesia.

Expt. 79 has very closely the same magnesia and lime ratios as 74 but was made from much more finely divided marl and was burned at a lower temperature. The amount of free magnesia indicated by the total expansion of 0.177 per cent. (bar 79 C) after four years as compared again with the 0.052 per cent. of bar 77 D indicates that the amount of free magnesia is the same as in Expt. 75, between 2 and 3 per cent. The burning temperature was about the same as 75 and the reason that the free magnesia is not higher is to be found in the finer subdivision of the raw material.

In view of the certain evidence of the presence of free magnesia in this cement, Expt. 79, special attention should be drawn to the fact that even the freshly burned cement stood perfectly the test of boiling a pat for twenty-four hours, and that neat briquettes showed a steady gain in strength from 575 pounds after twenty-eight days up to 911 pounds at the end of three years, with no apparent change at the end of the fourth year. This cement would then have passed all the physical tests required in the standard specifications adopted by the American Society for Testing Materials or the Board of Engineers of the United States Army. Yet it is now expanding at a rate which would arouse grave apprehensions had this cement four years ago been put into an important hydraulic undertaking in defiance of its high percentage of magnesia and relying solely on its good physical tests.

In conclusion and to show that much larger amounts of magnesia than those cited may be completely combined, reference may again be made to the all-magnesia cement, Expts. 80 and 82, which, made from finely ground materials and burned at a not unusually high temperature of 1496°, show not a sign of free magnesia.

EQUILIBRIUM BETWEEN FREE AND COMBINED LIME, AND FREE AND COMBINED MAGNESIA.

The lack of success experienced in making perfect cements with 4 and 7 per cent. magnesia was due in part to coarseness of

the raw materials in Expts. 74 and 75. The only reproach that can be brought against Expt. 79 is that a higher burning temperature might have produced better results. Yet it was burned hot enough to produce good clinker and a perfectly sound cement judged by all usual standards. It seems comparatively easy to get magnesia into combination in the presence of a small amount of lime as shown in Expts. 80 and 82, but when, as is the case in Portland cements, the amount of lime is many times greater than the magnesia it is probable that the more reactive lime enters into combination before the inert magnesia and that to the magnesia falls the task of displacing the lime until equilibrium is reached. When equilibrium is reached, unless both the lime and magnesia are completely combined, there should be *both* free lime and free magnesia present. Expts. 74 and 75 both show this condition, but on account of the coarseness of the raw materials, it is not safe to assume that the free lime is due to the attainment of equilibrium.

The better case of Expt. 79, when the raw materials are finer, shows free magnesia but fails to show free lime. This may be due to lack of delicacy in the test, for we have no means of judging in advance what percentage of free lime would correspond to equilibrium for a given temperature and proportion of magnesia. It seems, however, plausible that the time of passage through the rotary kiln is too short to allow the attainment of equilibrium, and that part of the magnesia remains uncombined on account of its inertness. Cements burned in fixed kilns like those made in Germany by Dyckerhoff would have a better opportunity to attain equilibrium. Yet Dyckerhoff was not able, except in one instance, to obtain perfect cements with over 4 per cent. of magnesia. Von Blaese was able with a fixed kiln to obtain cements with higher percentages, which showed themselves quite constant in volume. It is to be noted, however, that the clay used by him was lean, containing less than 40 per cent. as much R_2O_3 as SiO_2. We believe that the relatively large amount of silica and the long duration of burning furnished the best conditions for bringing the magnesia into the combined state.

Our experiments differ in that they were made in a rotary kiln, and although we are not prepared to state that sound cements cannot be manufactured in a rotary kiln when the raw materials contain large amounts of magnesium carbonate, we feel safe in

saying that if such cements can be manufactured, it will only be by paying the closest attention to the grinding of the raw materials and to the manner of burning, and that in the lack of a rapid test to determine the percentage of free magnesia it is far safer to stick to a 3 per cent. magnesia limit when the cement is to be used for important work under water.

The case of the influence of magnesia on cement seems to us to be parallel to the old discussion of the influence of phosphorus on steel. Many instances may be cited of steels high in phosphorus which have stood physical tests apparently satisfactorily. Yet engineers are unwilling to risk high phosphorus and are now insisting on a much lower percentage of that element in structural steel than was required a few years ago. It is now quite generally recognized among metallurgical chemists that the influence of an element such as phosphorus upon the properties of steel depends more upon the form in which that element exists than upon the total amount, and consequently if reliability is to be secured, the only safe course to follow is to require the objectionable element to be so low as to be harmless even if it exist in its most dangerous form.

The situation would be different provided the raw materials used contained magnesia already in combination with silica, as might be the case with some clays. An experiment has been made in this laboratory to determine how far lime would displace this harmless combined magnesia in burning a cement and throw the magnesia into the dangerous free form, but it has not been under observation years enough to enable us to give any judgment.

BEHAVIOR OF CEMENT BARS KEPT IN AIR.

In addition to the bars kept in water, duplicate bars of almost all these cements were kept on a shelf in a basement room of fairly constant temperature throughout the year, and measured regularly. The results of these measurements on bars left in air are given complete in Table IV and group the cements into two distinct classes, those that contain free lime, and those that do not contain free lime. The cements which do not contain free lime all contract in volume, and in a remarkably uniform manner, independent of composition. The smallest contraction noted at the end of four years is 0.300 per cent. and the highest 0.392 per cent. The larger figure is for a perfectly fresh cement (77 B)

and the lower is for the same cement aged six months (77 C). In the same way Expt. 81 shows a contraction on the aged cement of 0.300 per cent. (81 F and H) while the fresh cement (81 A) has a contraction of 0.382 per cent. Free magnesia exerts no measurable influence, the bars of Expt. 85 with added free magnesia up to 4 per cent. being indistinguishable from one another.

Almost all these bars show a fairly regular diminution in volume with the exception of a break between the third and sixth month when there is a slight expansion followed nearly always by a decided contraction at the end of one year. This is probably related to the phenomenon previously alluded to in the review of the behavior of bars kept in water. The changes of volume in bars kept in air and water are in general the reverse of each other, and the simultaneous breaks in the curves are probably more than accidental coincidence but we are not prepared at present to offer an explanation of the underlying causes.

The cements containing free lime are exemplified in Expts. 74, 75 and 78. Bar 78 B, containing 2.75 per cent. free lime, is the only instance of a cement known to contain free lime which was worked up fresh. During the first seven days the contraction was practically normal, but expansion due to hydration of the lime commenced to be evident after that date and continued to increase at an accelerated rate until at the end of nine months the bar had expanded 1.17 per cent. and had cracked so badly that observations were discontinued. Of the other cements known to contain free lime, bar 75 B, aged thirty days ground, showed a contraction for fourteen days followed by an expansion, which at the end of five years amounts to 0.800 per cent. The same cement (bar 75 C) stored seven months showed a normal behavior throughout, contracting regularly up to 0.330 per cent. at the end of four years. Bar 74 B, in which the cement was aged seven weeks as ground cement, still showed the influence of some free lime, for although at the end of five years its volume is less than it was initially by 0.059 per cent., yet this contraction is less than it should be for cement containing no free lime. This same cement, bar 74 D, aged seven and one-half months after grinding, shows a contraction almost as large as a normal cement.

The effect of free lime on cement bars kept in air is to cause expansion, not, however, noticeable until after twenty-eight days. The hydration of the hard-burned lime in air is so slow

that there may be continuous expansion up to five years or more. In case the amount of free lime is unusually high as in Expt. 78, the expansion may be great enough to cause disintegration. The normal behavior of cement bars is to contract in air and free magnesia exerts no measurable influence in this respect. Aging cement diminishes the contraction somewhat.

BEHAVIOR OF A CEMENT BAR ALTERNATELY IN WATER AND AIR.

It has been shown that cement bars stored in water normally expand and that bars stored in air contract. It is worth noting the effect of alternate exposure to air and water as bearing upon the behavior of cement sidewalks. A sample of clinker obtained from the same mill as Expts. 83 and 85 was stored in the laboratory for eight months and afterwards exposed to the weather for four months. The clinker was then ground with 1.5 per cent. plaster of Paris and the ground cement stored in the laboratory for five weeks. That this long aging had not caused any deterioration in the cement is shown by the fact that neat briquettes made at the time of the expansion bars gave a seven-day test of 420 pounds with increase of strength up to 737 pounds at the end of two years. From this cement two expansion bars were made and placed in water. 72 A kept in water showed very slight expansion as might have been expected from the long aging, the expansion at the end of four years being only 0.022 per cent.

Expansion bar 72 B was kept in water for four months and like 72 A remained almost constant in volume. It was taken out of the water and left in air for twenty-eight days when it contracted from —0.005 per cent. to —0.180 per cent. On being placed again in water, at the end of seven days it had expanded 0.150 to —0.030 per cent. and it remained practically constant for the next three weeks. It was again taken out of the water and placed in air and again contracted until at the end of twenty-eight days it had a contraction to 0.190 per cent., practically the volume which it had formerly assumed in air. It was now placed in boiling water for twenty-four hours and after cooling again showed an expansion to —0.030 per cent. as before after keeping in cold water.

This large alternate expansion and contraction as the result of alternate exposure to air and water gives some indications of the alternate strains to which cement walks are subject and may

easily account for the appearance of hair cracks so common in such structures, especially where a mixture very rich in cement is used as the top coating.

SUMMARY.

Free lime in Portland cement will not only not be slaked during the mixing and setting of the cement but will not become completely hydrated even when the cement is immersed in water, until about fourteen days have elapsed. The result of this gradual slaking is to produce abnormal expansion of the cement. Any evil effects due to the presence of free lime in cements kept under water will be manifested within two months. In case free lime is present in cement used in structures above ground or where it is usually dry, the expansion due to hydration of the cement will be more gradual but several times greater in volume than when the material is under water. The expansion due to free lime slaking in the air may become so great after several months as to cause complete disintegration.

The deleterious effects of free lime may be completely removed by aging the ground cement or storing the clinker to weather until the pat will stand a perfect boiling test. Weathering the clinker for three months is usually sufficient. It is difficult to state the length of time necessary to properly age ground cement to eliminate free lime. It will not ordinarily be less than one month and may be much longer according to the conditions under which it is stored.

Cement which passes a perfect boiling test may safely be assumed to contain no free lime. The expansion of a bar of neat cement containing no free lime when kept in cold water for seven days is usually under 0.040 per cent., but occasionally may go as high as 0.060 per cent. A cement with 2.8 per cent. free lime showed an expansion of 0.220 per cent. in the same period.

The effect of magnesia like that of lime depends less upon its total amount than upon the form in which it exists. Combined magnesia like combined lime has no injurious effect in Portland cement. Magnesia combined with silica and alumina forms a hydraulic cement which is safe but as compared with Portland cement is too weak to be of any commercial value. Free magnesia has no appreciable affect in cement used above ground where it is continuously dry. If the cement is wet for a part or a whole of

the time, the free magnesia will very slowly hydrate and cause expansion. Even where the cement is continuously immersed in water the expansion due to free magnesia is not appreciable until after two months and only becomes distinctly evident after a year. The hydration seems to be only well under headway at the end of the first year and expansion continues at an increasingly rapid rate for at least five years, and probably longer. Aging does not seem to diminish the deleterious effect of free magnesia in cement. This is to be expected, since the rate of hydration of hard-burned magnesia in air is almost imperceptibly slow.

The boiling test for twenty-four hours does not detect free magnesia as it does free lime. Cement containing as high as 4 per cent. of free magnesia has passed a perfect boiling test, yet the last measurement of this cement at the end of five years in cold water showed a total expansion of over 1 per cent., nearly half of which occurred during the fifth year after making.

This slow hydration of free magnesia with its accompanying expansion seems to be the probable cause of the expansion, frequently accompanied by more or less complete disintegration, so often noted in sidewalks, occurring several years after the walk has been laid.

One per cent. or less of free magnesia in cements kept under water causes little noticeable expansion even in neat cement; probably simply filling up the voids. Increased percentages of free magnesia cause cumulatively greater expansion until with 3 per cent. of *free* magnesia the expansion is too great to be at all safe.

In the manufacture of cement from raw materials containing magnesium carbonate, some portion of the magnesia will remain in the free state. This amount will increase with coarseness of raw materials, increasing percentage of lime and increasing percentage of magnesia. If the total magnesia does not exceed 3 per cent. it is not likely that well-made cement will carry enough of this magnesia in the free form to cause injurious expansion under any conditions of service. If the percentage of total magnesia rises above 3 per cent. there will be increasing probability of enough magnesia remaining in the free form to cause injurious expansion in large monolithic structures kept continuously or frequently wet. In structures where suitable provision can be made for expansion joints, a higher percentage of total magnesia is permissible than in monolithic structures. Magnesia should

TABLE II.—EXPANSION OF BARS OF NEAT CEMENT IN WATER.

All measurements represent percentage variation from original volume:
All measurements indicate expansion unless preceded by a — sign.

Expt.	No.	Days.				Months.							Years.				Remarks.
		7.	14.	21.	28.	2.	3.	4.	6.	9.	12.	18.	2.	3.	4.	5.	
74	A	0.190	0.226	0.240	0.240	0.290	0.310	0.330	0.350	0.363	0.370	0.423	0.447	0.499	0.550	0.582	Free CaO and free MgO.
	D	—0.005	+0.005	0.004	0.010	0.024	0.033	0.040	0.050	0.075	0.102	0.121	0.164	.....	0.245	.....	Aged. Free MgO.
75	A	0.200	0.240	0.265	0.270	0.305	0.315	0.330	0.350	0.355	0.355	0.383	0.390	0.407	0.370	0.432	Free CaO and free MgO.
	D	0.020	0.035	0.045	0.055	0.065	0.072	0.075	0.095	0.115	0.130	0.136	0.152	.....	0.177	.....	Aged. Free MgO.
77	A	0.038	0.055	0.060	0.070	0.098	0.112	0.120	0.135	0.132	0.130	0.163	0.158	0.170	0.180	0.190	Good cement used fresh.
	D	0.008	0.008	0.011	0.018	0.020	—0.005	—0.010	—0.005	+0.015	0.028	0.032	0.040	.....	0.052	.....	After aging.
78	A	0.220	0.260	0.280	0.295	0.340	0.355	0.363	0.385	0.390	0.390	0.414	0.412	0.421	0.441	0.451	Fresh. Free CaO.
79	A	0.025	0.045	0.050	0.070	.....	0.110	0.168	0.150	0.151	0.160	0.204	0.218	0.250	0.330	0.310	7.2 % MgO. Fresh.
	C	0.005	0.015	0.015	0.010	0.020	0.025	0.030	0.035	0.076	0.089	0.104	0.127	0.145	0.177	.....	7.2 " " Aged.
	E	—0.007	—0.001	—0.001	+0.003	.....	0.032	0.036	0.052	.....	0.095	0.117	0.140	0.180	.....	.....	7.2 " " "
80	A	0.022	0.030	0.040	0.040	0.040	0.040	0.040	0.050	0.032	0.032	0.057	0.062	0.082	0.100	0.102	All-magnesia. Fresh.
82	A	0.000	.....	0.005	0.008	0.010	0.025	0.010	0.025	0.010	0.010	0.029	0.040	0.059	0.080	.....	" Aged.
81	B	0.030	0.030	0.025	0.026	0.030	0.035	.....	0.045	0.063	0.077	0.082	0.090	0.099	0.105	.....	Same as 78, but aged.
	C	0.005	0.010	0.010	0.010	0.013	0.005	0.005	0.025	0.044	0.049	0.051	0.059	0.071	0.070	.....	" " 78, " "
	E	0.000	0.000	0.000	0.010	0.020	0.035	0.035	0.043	0.048	0.050	0.068	0.062	0.081	0.092	.....	" " 78, " "
	G	0.020	0.025	0.038	0.038	0.053	0.065	0.073	0.081	0.086	0.089	0.103	0.101	0.115	0.121	....	" " 78, " "

TABLE III.—EXPANSION OF BARS OF NEAT CEMENT IN WATER.

All measurements represent percentage variation from original volume.

All measurements indicate expansion unless preceded by — sign

Expt.	No.	Days.				Months.							Years.				Remarks
		7.	14.	21.	28.	2.	3.	4.	6.	9.	12.	18.	2.	3.	4.	5.	
83	A	0.030	0.038	0.045	0.055	0.080	0.100	0.080	0.090	0.090	0.100	0.112	0.116	0.132	0.139	0.144	Com. cement fresh.
	B	0.025	0.032	0.039	0.045	0.070	.....	0.075	0.082	0.075	0.095	0.106	0.117	0.134	0.144	0.146	" " " + 1% free MgO.
	C	0.020	0.030	0.040	0.050	0.073	0.094	0.075	0.096	0.078	0.113	0.133	0.150	0.170	0.190	0.203	" " " + 2% " "
	D	0.027	0.037	0.047	0.057	0.080	0.092	0.087	0.097	0.097	0.127	0.151	0.168	0.197	0.253	0.382	" " " + 3% " "
	E	0.030	0.040	0.052	0.065	0.090	0.110	0.104	0.120	0.120	0.158	0.172	0.223	0.290	0.562	1.010	" " " + 4% " "
	F	0.030	0.038	0.046	0.054	0.070	0.075	0.072	0.076	0.080	0.093	0.106	0.110	0.119	0.129	0.130	" " " + 1% comb. MgO.
	G	0.026	0.032	0.040	0.049	0.070	0.089	0.080	0.080	0.070	0.088	0.101	0.107	0.119	0.124	0.130	" " " + 2% " "
	H	0.025	0.036	0.045	0.055	0.060	0.079	0.070	0.070	0.070	0.090	0.101	0.106	0.118	0.130	0.138	" " " + 3% " "
	I	0.021	0.030	0.040	0.048	0.060	0.072	0.070	0.070	0.070	0.096	0.104	0.110	0.120	0.130	0.135	" " " + 4% " "
85	A	0.020	0.030	0.040	0.040	0.040	0.050	0.050	0.070	0.088	0.085	0.089	0.094	0.108	0.110	.....	Same cement aged.
	C	0.015	0.025	0.025	0.025	0.030	0.040	0.035	0.055	0.070	0.067	0.074	0.079	0.091	0.100	.....	" " "
	E	0.020	0.035	0.040	0.040	0.045	0.045	0.055	0.078	0.098	0.098	0.106	0.122	0.127	0.150	.....	" " " + 1% free MgO.
	G	0.025	0.035	0.035	0.035	0.055	0.048	0.065	0.085	0 106	0.107	0.124	0.135	0.154	0.165	.....	" " " + 2% " "
	I	0.010	0.030	0.035	0.040	0.035	0.055	0.060	0.085	0.110	0.115	0.136	0.154	0.185	0.240	.....	" " " + 3% " "
	K	0.020	0.035	0.040	0.040	0.055	0.060	0.080	0.103	0.134	0.141	0.175	0.199	0.282	0.615	.....	" " " + 4% " "
	M	0.020	0.025	0.030	0.030	0.043	0.045	0.060	0.070	0.084	0.082	0.093	0.096	0.109	0.115	.....	" " " + 1% comb. MgO.
	O	0.015	0.018	0.025	0.025	0.038	0.035	0.045	0.060	0.077	0.074	0.084	0.089	0.104	0.107	.....	" " " + 2% " "
	Q	0.000	0.015	0.015	0.015	0.030	0.030	0.040	0.058	0.072	0.070	0.080	0.087	0.108	0.099	.....	" " " + 3% " "
	S	0.002	0.002	0.002	0.003	0.005	0.012	0.022	0.032	0.054	0.052	0.062	0.069	0.081	0.084	.....	" " " + 4% " "

TABLE IV.—CONTRACTION OF BARS OF NEAT CEMENT IN AIR.

All measurements represent percentage variation from original volume.

All measurements indicate contractions unless preceded by a + sign.

Expt.	No.	Days. 7.	14.	21.	28.	Months. 2.	3.	4.	6.	9.	12.	18.	Years. 2.	3.	4.	5.	Remarks.
74	B	0.129	0.137	0.138	0.139	0.107	0.081	0.060	0.046	0.010	0.110	0.048	0.089	0.077	0.032	0.059	Contains free lime.
	D	0.015	0.055	0.085	0.135	0.178	0.196	0.205	0.205	0.210	0.200	0.259	0.244	.....	0.260	.....	Aged till free lime removed.
75	B	0.115	0.120	0.118	0.110	0.050	0.000	+0.095	+0.155	+0.100	+0.090	+0.240	+0.209	+0.342	+0.739	+0.800	Contains free lime.
	C	0.040	0.075	0.110	0.165	0.230	0.250	0.290	0.290	0.285	0.265	0.328	0.308	.....	0.330	.....	Aged till free lime removed.
77	B	0.190	0.220	0.227	0.237	0.240	0.237	0.232	0.240	0.318	0.355	0.314	0.355	0.383	0.392	0.393	Good cement used fresh.
	C	0.025	0.072	0.108	0.139	0.195	0.222	0.260	0.250	0.255	0.247	0.302	0.282	.....	0.300	.....	After aging.
78	B	0.120	0.110	0.100	0.085	+0.080	+0.320	+0.775	+1.110	+1.170	Bar badly cracked.						Contains free lime.
79	D	0.078	0.115	0.160	0.208	0.260	0.270	0.310	0.300	0.295	0.292	0.367	0.353	0.380	0.388	.....	7.2% MgO. Aged.
81	A	0.090	0.120	0.195	0.230	0.275	0.295	.....	0.335	0.315	0.306	0.365	0.355	0.380	0.382	.....	Same as 78, but aged.
	D	0.085	0.170	0.180	0.250	0.225	0.285	0.295	0.285	0.285	0.303	0.353	0.354	0.365	0.375	.....	" " 78, " "
	F	0.125	0.145	0.145	0.155	0.165	0.172	0.170	0.179	0.235	0.246	0.245	0.293	0.284	0.300	.....	" " 78, " "
	H	0.155	0.180	0.165	0.167	0.170	0.180	0.170	0.176	0.225	0.247	0.242	0.292	0.292	0.300	.....	" " 78, " "
85	D	0.107	0.165	0.180	0.210	0.260	0.260	0.270	0.265	0.265	0.316	0.335	0.366	0.378	0.385	.....	Commercial. Aged.
	F	0.100	0.150	0.170	0.180	0.217	0.220	0.217	0.210	0.204	0.249	0.262	0.307	0.322	0.335	.....	Com. Aged + 1 per cent. free MgO.
	H	0.135	0.185	0.195	0.205	0.235	0.255	0.240	0.240	0.225	0.273	0.286	0.324	0.337	0.355	.....	Com. Aged + 2 per cent. free MgO.
	J	0.105	0.150	0.160	0.190	0.230	0.225	0.220	0.217	0.206	0.253	0.263	0.305	0.319	0.335	.....	Com. Aged + 3 per cent. free MgO.
	L	0.110	0.170	0.170	0.200	0.240	0.240	0.240	0.235	0.229	0.274	0.290	0.325	0.346	0.360	.....	Com. Aged + 4 per cent. free MgO.
	N	0.110	0.168	0.178	0.203	0.233	0.230	0.223	0.238	0.228	0.272	0.287	0.323	0.334	0.358	.....	Com. Aged + 1 per cent. comb. MgO.
	P	0.110	0.160	0.175	0.195	0 230	0.220	0.230	0.235	0.225	0.272	0.290	0.325	0.339	0.355	.....	Com. Aged + 2 per cent. comb. MgO.
	R	0.120	0.165	0.180	0.200	0.225	0.220	0.210	0.225	0.218	0.257	0.277	0.313	0.325	0.350	.....	Com. Aged + 3 per cent. comb. MgO.
	T	0.110	0.160	0.180	0.190	0.210	0.200	0.200	0.220	0.217	0.264	0.278	0.313	0.311	0.330	.....	Com. Aged + 4 per cent. comb. MgO.

not exceed 5 per cent. total when used even under these circumstances.

An increasingly large amount of cement is being used in the structure of buildings where it will never be exposed to the action of water. There is no ground for believing that magnesia even in the free form would cause trouble under such circumstances. Free lime, however, is more dangerous in these structures than where the concrete is to be kept damp, because the expanding lime increases its volume much more in air than in water. Concrete made from sound cement will normally contract in the air, and this contraction continues according to our measurements for at least five years and amounts with neat cement to about four-tenths per cent. Whether this contraction will be sufficient to seriously weaken structures such as floors deserves investigation.

Any cement worked up fresh will change its volume more than if properly aged. It will show a noticeable drop in the curve representing change of volume after about three months, a period which corresponds to that in which briquettes show a falling off in tensile strength. Cement should always be aged for work where constancy of volume is of the highest importance. The only disadvantage of aging lies in the tendency for a cement to become very quick-setting. If it is aged long enough, it reverts again to a slow-setting cement.

Leaving out of account free lime and magnesia the amount of expansion of a cement is apparently dependent upon the proportion and arrangement of the other constituents. The experiments here reported deal with cements with fairly low lime, and with alumina and oxide of iron also below rather than above the average. We have made cements richer in alumina and oxide of iron and also in lime, but observations have not as yet been carried out for a long enough period of years to warrant generalization. The data so far gathered confirm the general results given above but indicate that these cements higher in lime and alumina will be less constant in volume than those described here.

UNIVERSITY OF MICHIGAN,
ANN ARBOR, July, 1906.

ON THE HEAT-TREATMENT OF SOME HIGH CARBON STEELS.[1]

By William Campbell.

Received July 17, 1906.

TABLE OF CONTENTS.

Introduction 1304
Previous work on the subject 1305
Outline of present work 1305
Material used 1305
Heat treatment 1306
Mechanical tests 1307
Summary of results of mechanical tests 1307
Maximum load 1307
Elastic limit 1310
Reduction of area 1313
Elongation 1313
Fractures of test-pieces 1313
Examination of microstructure 1316
Structure of the original steels 1316
Changes of structure in steels 1 to 4 1317
Changes of structure in steels 5 and 6 1320
Effect of heat-treatment upon the structure and its bearing on the mechanical properties 1320
Conclusion 1321

Introduction.—The study of steel and the changes which it undergoes forms one of our most important lines of research at the present day. Our knowledge of the subject has made great advances during recent times and we now know the reason for many of the profound changes of structure and of constitution which take place with changes of temperature. This advance is due in a great measure to the great improvements in pyrometry, to the wide application of metallography and to the use of certain principles of physical chemistry in explaining our results.

From a constitutional point of view steel naturally falls into three groups:

(1) Unsaturated (Arnold): Hypo-eutectoid (Howe), consisting of ferrite and pearlite in the slowly cooled condition. Carbon content less than 0.9 per cent.

(2) Saturated: eutectoid, consisting of pearlite alone. Carbon about 0.9 per cent.

[1] Work carried out in conjunction with Committee F on the "Heat-Treatment of Steel," American Society for Testing Materials.

(3) Supersaturated: hyper-eutectoid, consisting of cementite and pearlite in the normal condition. Carbon content greater than 0.9 per cent.

Previous Work on the Subject.—Since Osmond's classic paper[1] on the transformations of structure which take place within the range of the critical points of steel, a vast amount of research has been done. In many cases both high, medium and low carbon steels have been studied and the work of Arnold,[2] Sauveur[3] and Stead[4] has thrown much light on the subject. In other cases, the effect of varied heat treatment on the physical properties and microstructure of some particular steel has been worked out. Fay and Badlam[5] worked with a low carbon steel of 0.07 per cent. carbon and 0.32 per cent. manganese. Morse[6] used a medium carbon, 0.34 per cent. with 0.22 per cent. manganese. Campbell[7] studied a rail steel with 0.5 per cent. carbon and 0.98 per cent. manganese, while Sargent[8] took up the subject with a high carbon steel (1 per cent. carbon).

The Sixth Report of the Alloys Research Committee[9] deals with the heat treatment of a series of eight steels (0.13 to 1.3 per cent. carbon) at temperatures from 620° to 1100°, and works out their mechanical properties and microstructure.

The present work was undertaken along similar lines because there seemed an opening for research work on steels high in carbon.

Outline of Present Work. Crucible Steel.—A series of six steels,[10] $^5/_{16}$ inch square, whose analyses are given in Table A were used in the form of 12-inch test pieces. Heats were made in a horizontal cylindrical gas forge. The bars were packed in an inner iron tube 2 inches in diameter which was then placed in the axis of a larger tube $3\frac{1}{2}$ inches in diameter by means of which heating was done by radiation and was very uniform.

[1] Bull. Soc. d' Euc. 1895, 10, 476 (Osmond and Stead: "Microscopic Analysis of Metals," Lippincott).

[2] J. Iron and Steel Inst. 1901, 1, 175, 1905 2, 27.

[3] Trans. A. I. M. E. 1896, p. 863, etc.

[4] J. Iron and Steel Inst. 1898 1, 145, etc.

[5] Tech. Quart. 1900.

[6] Trans. A. I. M. E. 1899, 729.

[7] J. Iron and Steel Inst. 2, 359 (1903).

[8] Trans. A. I. M. E. 1901, 303.

[9] Inst. Mech. Eng. London, 1904.

[10] The gift of the Carpenter Steel Co., to whom our thanks are due.

The furnace was charged cold and the heating was so regulated that the maximum temperature was reached in about one to one and a half hours. As soon as the temperature was steady, say five minutes, the gas and blast were turned off and the furnace allowed to cool slowly. This took three and a half or more hours.

An exact record of heating and cooling was kept by means of a LeChatelier pyrometer, the hot junction being in the center of the bundle of steels.

Nine heats were made between 650° and 1200°. The temperatures and heat numbers are given in Table B. These temperatures are very close to those aimed at, *viz.*, 650°, 710°, 750°, 800°, 850°, 900°, 1050° and 1200°.

The critical points of each steel had been previously taken and on heating Ac_1 lay between 730° and 740° while on cooling Ar_1 was found to be 710° to 700°. Ac_{2-3} and Ar_{2-3} were not detected, however. The above temperatures were therefore chosen so that one heat was below the critical points, one was at Ar_1, a third just above Ac_1 *i. e.*, to the region where the change from pearlite into the solid solution is complete. The heats to temperatures above this pass through the region of the change Ac_{2-3} or the solution of cementite (iron carbide) in the solid solution, 1200° producing great overheating.

TABLE A.—ANALYSIS OF STEELS.

No.	C.	Mn.	P.	Si.	S.
1	2.04	0.28	0.014	.....	0.014
2	1.94	0.20	0.009	0.17	0.013
3	1.72	0.075	0.013	0.20	0.018
4	1.61	0.19	0.013	0.19	0.013
5	1.04	0.12	0.012	.....	0.017
6	0.70	0.068	0.012	0.141	0.019

TABLE B.—HEAT TREATMENT.

Heat No.	Heated to °C.
3	650
1	715
6	760
2	800
4	855
0	905
5	950
2	1070
8	1200
A	As rolled.
X	

All of the heats reached their maximum in one to one and one-half hours with the exception of Z to 1070° which took two hours and twenty minutes to heat up. This was due to trouble with the blast.

The mechanical tests were made on a Riehlé testing machine,[1] the elastic limit being determined by drop of the beam and elongation measured in 2 inches.

The figures thus obtained have been tabulated in Tables I to IV and from these tables have been plotted curves I to IV. Instead of following the usual custom and plotting the figures for each steel on a separate sheet, it was found that by making four tables and four curves to correspond, for (1) maximum loads, (2) elastic limits, (3) reductions of area, (4) elongations, a great deal more could be learned of the changes as a whole.

Summary of Results of Mechanical Tests.—From an examination of the mechanical properties, microstructure and fractures, it was immediately seen that the steels fell naturally into two groups, *i. e.*, those consisting of pearlite with an excess of cementite or Nos. 1 to 4 and those consisting of pearlite alone (or nearly so), Nos. 5 and 6. It will be noticed how markedly the curves follow the same general directions and tend to coincide with each other.

Maximum Load. Table I, Curve I.—Of the first four steels, No. 4 with 1.61 per cent. carbon is the strongest with 160,000 pounds per sq. in. The weakest is No. 1 with 144,000 pounds per sq. in. Heating to 650°, which is far below the critical point, causes a reduction of some 30,000 pounds, while heating to a temperature just above the critical point Ac_1 (760°) brings down the maximum load to approximately the same point for each steel, *viz.*, between 95,000 and 100,000 pounds per sq. in. Heating to higher temperatures has but little further effect until we reach heat 8, 1200°, where the maximum load has dropped sharply some 25,000 to 40,000 pounds and now lies between 70,000 and 58,000 pounds per sq. in. In this heat, as in the case of the bars as rolled, No. 1 is the weakest and No. 4 strongest.

Of the last two steels as rolled, No. 5 with 1.04 per cent. carbon has maximum load of 140,000 pounds and No. 6 with 0.70 per cent. carbon has maximum load of 117,000 pounds per sq. in.

[1] Thanks are due to Professor Woolson, Columbia University, for use of this machine.

TABLE I.—MAXIMUM LOADS IN THOUSAND POUNDS PER SQUARE INCH.

Steel. No.	Carbon. Per cent.	As rolled. A.	As rolled. X.	Heat number and maximum temperature in ° C. 650°. 3.	715°. 1.	760°. 6.	800°. 2.	855°. 4.	905°. 0.	950°. 5.	1070°. Z.	1200°. 8.
1	2.04	144.6	144.0	115.4	114.5	98.8	95.6	93.8	95.2	95.2	99.0	57.4
2	1.94	146.5	146.3	115.2	104.1	95.0	92.0	89.2	95.3	91.8	97.0	61.3
3	1.72	152.8	154.0	126.0	114.1	100.3	98.0	94.0	94.3	95.0	92.3	65.3
4	1.61	162.2	153.2	128.1	117.0	98.6	97.7	95.0	97.3	96.3	94.4	69.8
5	1.04	140.6	141.6	105.4	97.8	86.8	96.6	111.8	115.9	111.5	106.1	112.6
6	0.70	117.4	116.6	95.2	88.7	85.6	94.3	91.3	90.3	90.5	89.5	90.0

TABLE II.—ELASTIC LIMIT IN THOUSAND POUNDS PER SQUARE INCH.

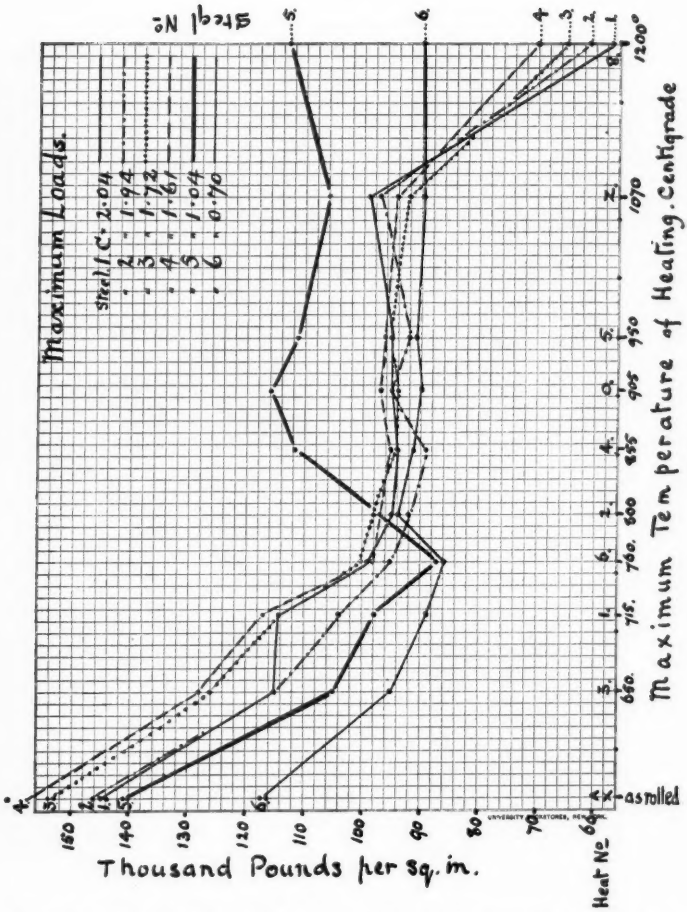
Steel. No.	Carbon. Per cent.	As rolled. A.	As rolled. X.	Heat number and maximum temperature in °C. 650°. 3.	715°. 1.	760°. 6.	800°. 2.	855°. 4.	905°. 0.	950°. 5.	1070°. Z.	1200°. 8.
1	2.04	101.8	104.2	84.6	83.9	57.7	57.8	55.5	55.3	49.3	49.6	56.0
2	1.94	91.0	91.5	72.6	68.6	50.5	51.0	49.4	49.8	41.7	47.0	....
3	1.72	98.7	97.5	78.3	75.7	50.5	48.7	47.9	48.6	45.2	43.1	50.6
4	1.61	105.2	105.2	85.3	81.3	52.3	53.3	51.3	51.3	48.5	51.4	....
5	1.04	75.8	75.8	57.7	55.2	44.8	46.6	47.2	50.6	46.8	56.5	89.6
6	0.70	65.3	64.2	53.2	49.7	40.2	42.1	42.1	41.4	39.7	57.3	58.5

TABLE III.—REDUCTION OF AREA PER CENT.

Steel. No.	Carbon. Per cent.	As rolled. A.	As rolled. X.	Heat number and maximum temperature in °C. 650°. 3.	715°. 1.	760°. 6.	800°. 2.	855°. 4.	905°. 0.	950°. 5.	1070°. Z.	1200°. 8.
1	2.04	3.5	3.0	6.5	6.6	16.2	19.6	13.2	12.6	5.8	2.7	0.4
2	1.94	6.5	6.0	8.9	12.0	18.8	15.0	12.1	9.5	12.0	7.6	1.4
3	1.72	5.2	8.7	7.3	18.8	20.5	10.3	12.0	9.6	6.3	4.3	1.0
4	1.61	8.2	9.1	8.3	21.5	34.0	19.1	14.2	9.4	6.8	2.6	1.9
5	1.04	22.7	21.8	36.2	41.5	36.6	21.0	11.3	8.8	10.9	10.6	10.7
6	0.70	27.3	27.0	33.9	45.2	38.7	20.9	20.7	21.8	20.5	17.9	16.8

TABLE IV.—ELONGATION IN TWO INCHES.

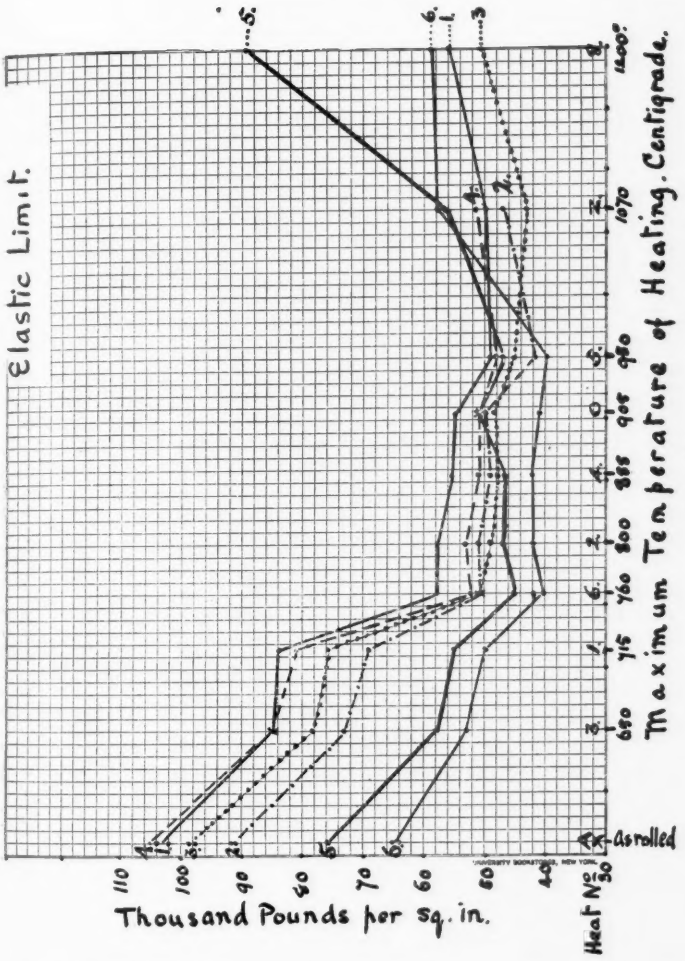
Steel. No.	Carbon. Per cent.	As rolled. A.	As rolled. X.	Heat number and maximum temperature in °C. 650°. 3.	715°. 1.	760°. 6.	800°. 2.	855°. 4.	905°. 0.	950°. 5.	1070°. Z.	1200°. 8.
1	2.04	4.5	4.0	6.0	7.0	11.5	12.5	12.0	11.5	6.0	4.5	1.0
2	1.94	6.0	6.5	8.0	9.5	15.0	17.0	12.5	7.0	9.5	8.5	2.0
3	1.72	6.5	8.0	8.0	11.5	16.5	10.0	13.5	11.0	7.5	6.0	2.0
4	1.61	7.0	6.0	..	14.5	20.0	18.5	15.0	11.5	7.5	3.5	3.0
5	1.04	13.5	12.0	18.0	22.0	26.5	19.0	13.0	13.0	10.5	11.0	11.5
6	0.70	17.0	17.0	23.0	27.5	27.0	19.0	18.5	18.0	16.5	18.0	16.0



Curve I.

Heating to 650° and 715° brings down the strength regularly as before, while the 760° heat (just above Ac_1) gives the same maximum load of 86,000 pounds per sq. in. for both. In the case of steel No. 5, heating to higher temperatures causes a great rise in strength with a maximum of 116,000 pounds for heat No. 0 (905°). For steel No. 6 the improvement is slight but permanent.

Elastic Limit. Table II, Curve II.—For the first four steels the curves have the same general form as for the maximum loads.

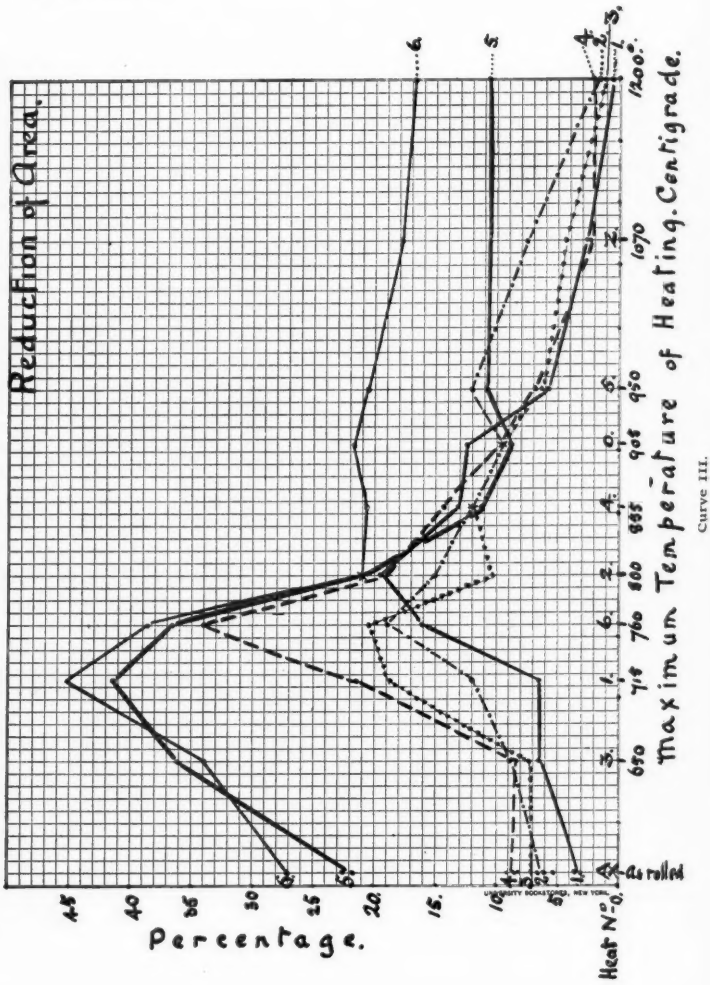


Curve II.

In all, heating to 650° brings about a fall of some 20,000 pounds; heating to 715° gives a slight but regular decrease, while the bars heated to just above the critical point (heat 760°) had an elastic limit down to 50,000–58,000 pounds per sq. in. for steels 1 to 4. For steels 5 and 6 this occurs at 44,800 and 40,200 pounds

per sq. in. In the 950° heat, the elastic limit for all of the steels occurs between 40,000 and 50,000 pounds per sq. in.

As in the maximum loads so here heating to higher temperatures (1070° and 1200°) causes an improvement both for steel 5 and steel 6.



Curve III.

Reduction of Area. Table III, Curve III.—In general we find that the ductility increases as the strength falls off. For steels 1 to 4 the reduction of area increases till a maximum is reached for the heat just above the critical point, 760° (in case of steel 1 800°). In the case of steel 4, C = 1.61 per cent., the rise is from 8.2 to 34 per cent., showing some marked change in the structure of the steel.

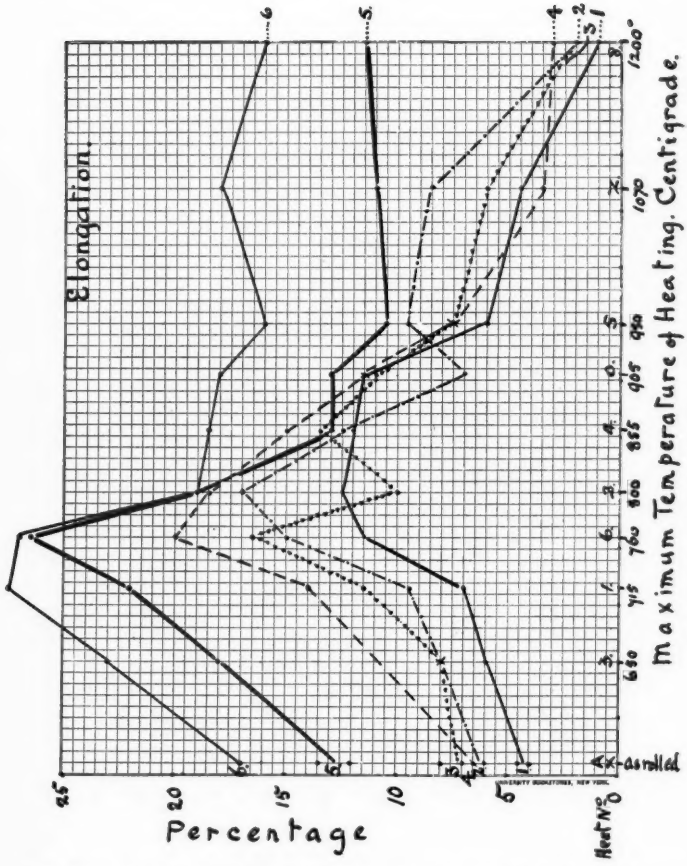
For steels 5 and 6 the maximum occurs in heat 1 to 715°, being almost double that of the bars as rolled. The 760° heat shows a slight fall, but the next heat (800°) shows a fall to 21 per cent., or less than half the maximum. Beyond this point No. 6 shows but little further change, being overheated. No. 5 falls away to about 11 per cent. with the next heat (855°) and then remains constant. It is likewise overheated.

For steels 1 to 4 the 855° heat has produced a fall to between 12 and 14 per cent., while further heating produces a uniform decline to less than 2 per cent. for the 1200° heat. At this point as in the bars as rolled the figures, with one exception, run in the order of carbon content. The irregularity of steel 3 heat 2 to 800° in this and the elongation is due to fracture occurring in the grips.

Elongation in 2 Inches. Table IV, Curve IV.—Heating up to a certain point increases the elongation as well as the reduction of area. The maximum for steels 1 and 2 is found in the 800° heat, for steels 3, 4 and 5 in the 760° heat, while for steel 6, the 715° heat gave a slightly higher figure. As in the case of the reduction of area so here we find that heating to higher temperatures causes a falling off. Steel 6 at 800° and steel 5 at 855° are badly damaged, and further heating has but little further effect. Steels 1 to 4 show a regular falling off until with the 1200° heat the elongation lies between 1 and 3 per cent. (steel 2, heat 0 to 905° is irregular, due to breaking in the grips). As we should expect, there is a very close resemblance between the curves for elongation and those for reduction of area.

Before attempting to explain the above changes which occur in the physical properties around the critical point Ac_1 and elsewhere, it seems best to examine both the fractures and microstructure, when it will be seen that here again we have profound changes taking place at the same points.

Fractures of Test-pieces.—In Fig. 1 we have the whole of the fractures assembled in pairs in such a way that each horizontal



Curve IV.

row (of pairs) corresponds to one steel varying in heat treatment from right to left; each vertical row on the other hand represents one heat and contains 6 different steels. In Figs. 2 to 13 typical fractures are shown, magnified 6 diameters.

Steel 1, C = 2.04 per cent.—In Fig. 1 there are two changes noted in steel No. 1. The finest fracture is from heat 2 at 800°. Up to this point there is but little change and Fig. 6 may be taken as the type. From heat 2 onwards to heat 5 at 950° there is a progressive coarsening of the grain and the appearance of a thin

crystalline border (Fig. 2). Heat Z shows a great change, for the fracture is very coarse and shows up black, with a strong columnar border. This is even more marked in heat 8, 1200°, where the border is one-third of the radius. Figs. 5 and 9 serve as types.

Steel 2, C = 1.94 per cent.—The finest fracture occurs in heat 6, 760°, beyond which the grain gets coarser. At heat 5, 950°, in addition to the bright crystalline border there is a marked zone just beneath the surface which is black from graphite. The change can be seen by comparing Figs. 2 and 3. Heating to 1070°, heat Z, completes this precipitation of graphite and the fracture is coarse throughout as in Fig. 4. Fig. 5 shows the fracture of the 1200° heat which is still more coarse, with the strong columnar border as before.

Steel 3, C = 1.72 per cent.—Fractures of heats 1 and 6 are very fine. Fig. 6 shows the fracture as rolled and may be taken as the type of these first three steels. Fig. 7 shows that of the 715° heat and is also a type. With increase in temperature above the critical point the fractures grow coarser and the crystalline border shows more and more. Heat Z again shows the marked change to a very coarse fracture throughout, with a strong columnar border, as is shown in Fig. 8. Fig. 9 shows the fracture for the 1200° heat, just as coarse but of lighter color; no graphite.

Steel 4, C = 1.61 per cent.—The smallest fracture is that of heat 6, 760°, which is also the finest. Above this point we get a gradual coarsening of the grain with the great change at 1070°, due to marked overheating, as in steel No. 3. There is but little graphite in Z, however. The 1200° heat shows the change in color, no graphite present.

Viewed as a whole steels 1 to 4 show the finest fracture just above the critical point. From this point onwards the grain grows coarser and a thin crystalline border shows, which as we shall see later is most probably due to decarburization. At heat Z, 1070°, all the fractures become coarse throughout, with a strong columnar border and black color due to graphite. Heat 8, 1200°, gives an even coarser fracture and the border is at least one-third radius deep. Steels Nos. 3 and 4 also show a change in color at this heat, due to the absence of graphite.

Steel 5, C = 1.04 per cent.—The assembled fractures for this steel (Fig. 1) show a marked change. As rolled the fracture shows

Curve IV.

a dark core as seen in Fig. 10. Heating to 650° yields a smaller fracture shown in Fig. 11. Heat 1 to 715° gives the finest fracture, and this is shown in Fig. 5. The 760° heat also yields a fine fracture but in heat 2, 800°, there is considerable coarsening. Heating to 855° causes a marked change and produces a coarse fracture throughout, showing that overheating occurs here. From this point on the fractures are all coarse and Fig. 13, heat Z to 1070°, may be taken as a type.

Steel 6, C=0.70 per cent.—The assembled fractures are very similar to those of the last steel, the 715° heat yielding the finest fracture. Overheating, however, is seen to occur at 800°. The dark center of the bar as rolled (as in Fig. 10) continues to heat 6 at 760°. This is apparently due to the outer part of the bar rupturing across the grain while the core breaks like fibre. Thus in steels 5 and 6 overheating occurs at such low temperatures as 855° and 800°. The finest fracture is given by the 715° heat. However, it may be remarked that the finest fracture does not necessarily mean the finest grain in the steel. Reduction of area has taken place and so in steels having grains of equal size, the one with the greater reduction of area would apparently have the finer grain as judged by fracture. When the microstructure is taken into account it is seen that the grain from the 760° heat is as fine as, if not finer than, any other.

Examination of Microstructure.—Sections were cut from each bar, ground down on an emery wheel, rubbed on emery papers and finally polished with broadcloth and rouge, as has been described in detail elsewhere.[1]

It was found that either a 2 per cent. solution of nitric acid in alcohol or a 5 per cent. picric acid in alcohol developed the structure in a very satisfactory manner.

To observe the general changes which take place a power of 44–88 diameters is used in an ordinary microscope in conjunction with a Sorby-Beck illuminator.[1] Then for more detailed work a higher magnification of 260–500 diameters was obtained by using a LeChatelier stand. Over 100 photographs were taken to record the various changes which take place. By choosing types, however, these have been represented by Figs. 14 to 25.

Structure of the Original Steels as Rolled.—Steel 1 consisted of

[1] Stead: Cleveland Inst. Engineers, February 26, 1900; Campbell: School of Mines Quart. 25, 390.

both patches and veins of cementite in a groundmass of pearlite, much of which is in the sorbitic condition. In a longitudinal section the patches of cementite are drawn out, while at the edge of the specimen the pearlite grain with its cementite envelope is elongated in the direction of rolling. Hence we may judge that rolling was finished after the cementite had begun to separate out, *i. e.*, in region of Ar_{2-3}. The comparatively rapid cooling of bars of $^5/_{16}$ inch cross-section would produce pearlite in the sorbitic or unsegregated condition.

Steel 2 is similar but contains fewer patches of cementite.

Steel 3 consists of medium-sized grains of pearlite surrounded by irregular envelopes of cementite, and practically no patches as occur in Nos. 1 and 2. The pearlite varies from well-laminated to sorbitic.

Steel 4 shown in Fig. 14 ×260 has a structure similar to steel 3.

Steel 5 as rolled consists of pearlite alone in medium-sized grains, whose texture varies from very fine to coarse.

Steel 6 shows some ferrite at the surface. The rest of the section consists of medium-sized grains of pearlite with very thin films of ferrite which disappear towards the center. Much of the pearlite is sorbitic.

As in the case of the physical properties and fractures the steels naturally fall into two groups, (1) steels 1 to 4 and (2) steels 5 and 6, according to their carbon content.

Changes of Structure in Steels 1 to 4.—Such heat treatment as the steels have undergone produces more or less decarburization. This first shows in heat 6, 760°, becomes more visible in the heat to 800° and probably gives the crystalline border to the fracture, while at 1200° it has penetrated deep into the steel. This is shown in Fig. 17 ×44, which is taken from the corner of steel 1 heat Z, 1070°. On the left-hand side we see the normal structure, globular cementite in pearlite, while the center of the photograph consists of pearlite alone, 0.9 per cent. carbon. At the extreme right ferrite makes its appearance at the corner of the specimen and the carbon content falls below 0.4 per cent. The same change through decarburization occurs in steels 5 and 6.

Change in the Pearlite.—In the bars as rolled the pearlite is either very finely laminated or in the sorbitic condition. Heating to even 650° causes a change and the pearlite tends to become granular, the cementite drawing up into globules which polish

in relief. The higher the temperature up to the critical point the stronger the segregation of the cementite of the pearlite. The size of grain of the pearlite, however, does not show any apparent change, until the critical point Ac_1 is passed, when the steel is refined as regards the pearlite. Heating to temperatures above this point produces larger and larger grains of coarser and coarser pearlite. The coarseness depends on the rate of passing through Ar_1 which was comparatively slow in these experiments. The size of grain as rolled is given in Fig. 14×260. That of steel No. 3 heated to 1200° is given in Fig. 23×44 diameters only, and is over ten times as great.

Change in the Cementite.—As rolled the cementite occurs as veins or patches more or less drawn out in the direction of rolling. Heating to 650° or above causes these veins to break down, due to the tendency for the cementite to take a globular form. The higher the temperature the greater the segregation. Fig. 15×260 shows steel No. 3, heat 2 to 800°, while Fig. 16 shows steel No. 2, heat 5 to 950°, in which globules of cementite have become very coarse indeed. Figs. 14, 15 and 16 illustrate the complete change very well indeed; but as the temperature rises above the critical point Ac_1 (therefore in all heats above 760°) the cementite also tends to dissolve in the solid solution formed by the transformation of the pearlite (and called austenite, martensite, hardenite, etc.). On cooling down again all of this dissolved cementite separates out, as a rule on the undissolved grains of cementite but lacking these, around the grain of the solid solution as an envelope. Arnold,[1] on the other hand, maintains that cementite only dissolves in the solid solution (hardenite) when the temperature has become a little above 900° and on cooling falls out of solution completely at about 900°. He also "advances the proposition that the Fe_3C of cementite and the Fe_3C of pearlite are physically different substances though identical in chemical composition."

As the temperature rises a point is reached where any cementite which remains undissolved breaks down into ferrite and graphite. As a rule we find a kernel of graphite with a skin of ferrite, but this latter may dissolve in the solid solution. Fig. 18×260 shows the center of steel No. 1, heat 8 to 1200°, while Fig. 20 shows steel No. 2, same heat, from near the side. These sections show only ferrite

[1] Arnold: J. Iron and Steel Inst. 1899, 1, p. 85; 1905, 2, 27.

and graphite in a groundmass of pearlite and little or no cementite has been dissolved. Outside this graphite zone, however, the cementite has all dissolved and on cooling has separated as seen in Figs. 19 and 21. Fig. 19×260 shows outer zone of steel No. 2, heat 8 to 1200°, and Fig. 21×44 shows outer zone of steel No. 1, same heat, in which all of the cementite has separated out as veins and as sheets within the very coarse grain of the pearlite. This zone lies between the central core and the outside decarburized covering, and seems to show the beginning of the next change.

In the case of steels 3 and 4 the change of cementite into ferrite-graphite kernels occurs at 1070° or lower. When these steels are heated up to 1200° the whole of the cementite is taken into solution and separates out again on cooling as is shown in Figs. 23, 24 and 25. Fig. 23×44 diameters shows steel 3 heated to 1200° and slowly cooled, consisting of very coarse grains of pearlite surrounded by irregular envelopes of cementite, some of which has separated out within the grain as is characteristic of overheated material. (Fig. 24×44 oblique illumination shows up the change in color by changing the light from vertical to oblique, and now the pearlite appears light and the cementite dark.) Fig. 25×44 shows steel No. 4 heated to 1200° which is similar to the last but has a much smaller grain. The wavy irregular appearance of the cementite is well shown in Fig. 22×260 steel No. 3 heated to 1200°. The photo is taken from near the edge of the specimen.

To sum up, we find two changes taking place. The first occurs at a constant temperature, the change Ac_1 the transformation of the pearlite. The second is the change in the cementite. Heating causes the cementite to segregate, the higher the temperature the greater the segregation. At a certain temperature which differs in the different steels this segregated cementite breaks down into ferrite and graphite.[1] In steel No. 1 this occurs at 1200°, began at 950°, was marked at 1070° and complete at 1200° in steel No. 2. In steel No. 3 it was complete at 1070° while in steel No. 4, though not showing at 950°, the 1070° heat shows it together with the next change. Lastly, we have the complete solution of the cementite, the temperature of which also varies. In steels Nos. 1 and 2 this occurs above 1200°, in steels Nos. 3 and 4 it occurs at

[1] According to Arnold and McWilliam (J. I. S. I. 1905, 2, p. 47), this change takes place on cooling and occurs at a low red heat.

1200°, though steel No. 4 shows it beginning at 1070°. This dissolved cementite separates out on cooling as an irregular envelope to the pearlite grains.

These changes are of the utmost importance in the making of malleable castings, as well as in the manufacture of cutlery, etc. It must be added here that in different parts of bars of steels Nos. 1 and 2 as rolled traces of graphite were found in the center, and evidently formed during the rolling. These persist and are found in the 1070° heat, but for the sake of clearness they have not been considered here.

Change of Structure in Steels 5 and 6.—The changes which take place in the pearlite by heating up to the critical point are the same as described above.

Steel 5, C=1.04.—Heating to 800° causes a growth in the pearlite grain and allows the cementite in excess of the eutectoid ratio (0.9 per cent. carbon) to separate out as a thin film round the pearlite grain. Heating to 855° so coarsens the pearlite that the steel is overheated. The cementite film has disappeared.

Steel 6, C=0.70 per cent.—Heating up to the critical point in places produces a marked segregation of the cementite of the pearlite resulting in coarse lamination. Heating to 800° causes a great increase in grain size and the film of ferrite, seen in the section as rolled, has now changed to grains. The steel is overheated at this low temperature.

Effect of Heat Treatment upon the Structure and Its Bearing on the Mechanical Properties.—From the above work it is noted that heating to temperatures up to the critical point Ac_1 in general, increases the ductility at the expense of the strength. The fractures show no marked change in size of grain till the critical point is reached, though of course they decrease in area. Under the microscope this is explained by (1) the breaking down of the veins of cementite and its segregation, tending to take a globular form and (2) a change in the character of the pearlite. The size of grain of the pearlite does not change until the critical point has been passed and it is therefore necessary to heat to a point just above Ac_1 for complete refining.

In the case of the steels high in carbon (1 to 4) the strength, as compared with that of the refined bars, is changed but little on heating to higher temperatures, until at the maximum tem-

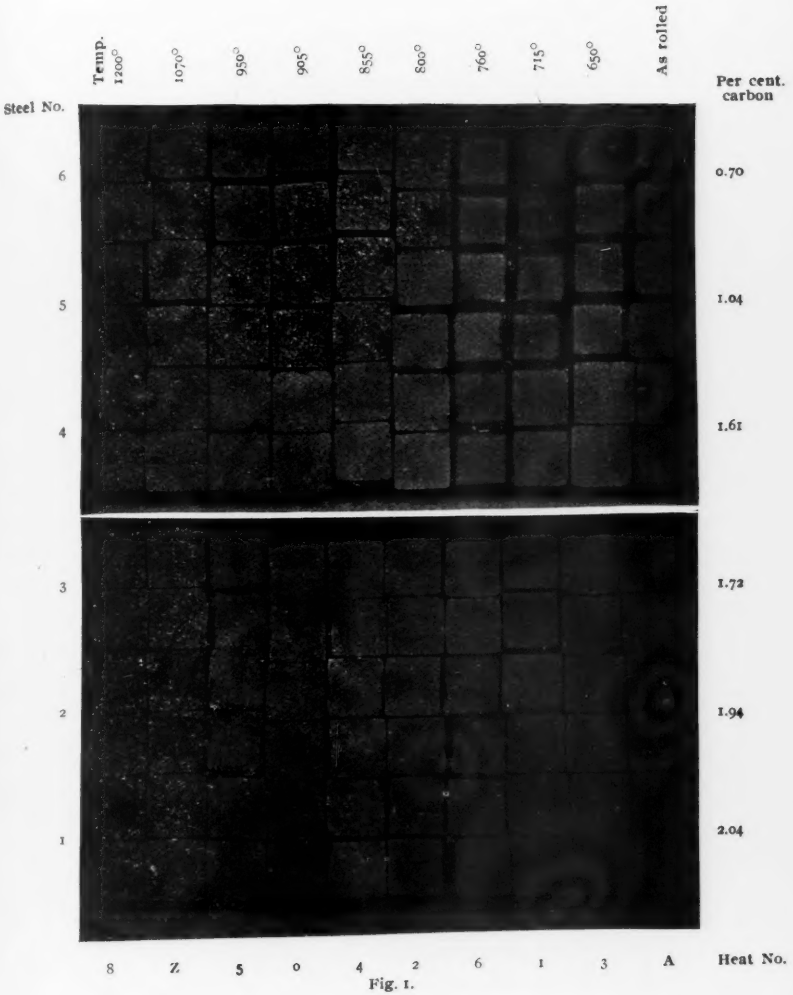

Temp. 1200°
1070°
950°
905°
855°
800°
760°
715°
650°
As rolled
Steel No.
Per cent. carbon
6
0.70
5
1.04
4
1.61
3
1.72
2
1.94
1
2.04
8
Z
5
0
4
2
6
1
3
A
Heat No.

Fig. 1.

Fig. 5. Steel 2, heat 1200°.

Fig. 6. Steel 3, as rolled.

Fig. 7. Steel 3, heat 715°.

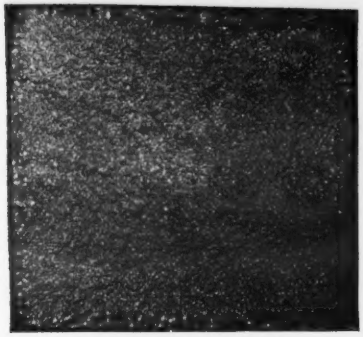


Fig. 2. Steel 2, heat 905°.

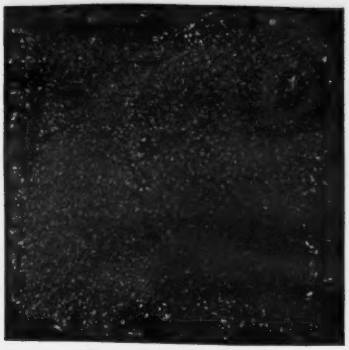


Fig. 3. Steel 2, heat 950°.

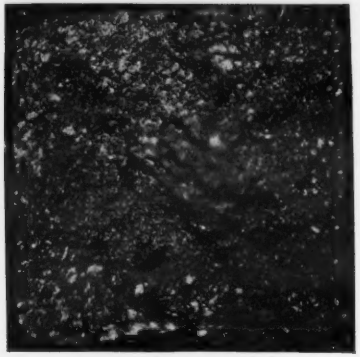


Fig. 4. Steel 2, heat 1070°.

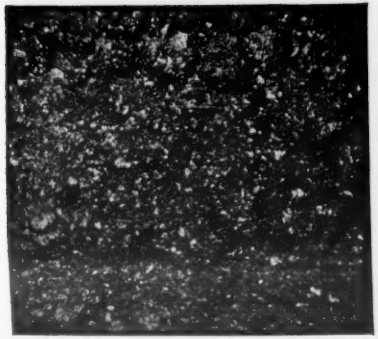


Fig. 5. Steel 2, heat 1200°.

Fig. 6. Steel 3, as rolled.

Fig. 7. Steel 3, heat 715°.

Fig 11. Steel 5, heat 650°.

Fig. 12. Steel 5, heat 715°.

Fig. 13. Steel 5, heat 1070°.

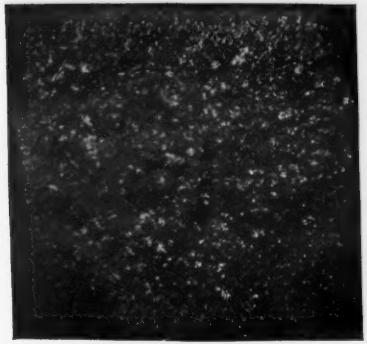


Fig. 8. Steel 3, heat 1070°.

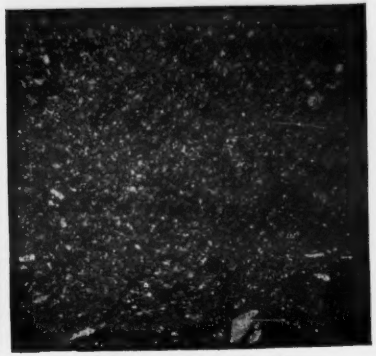


Fig. 9. Steel 3, heat 1200°.

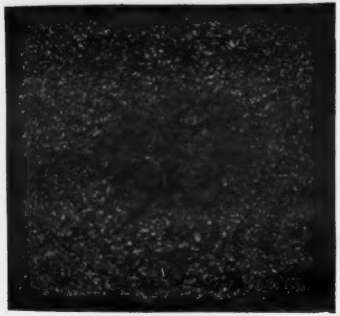


Fig. 10. Steel 5, as rolled.

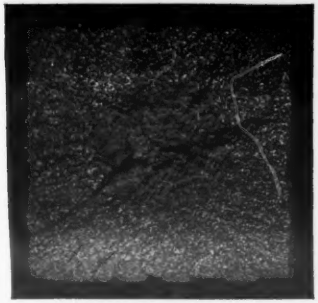


Fig 11. Steel 5, heat 650°.

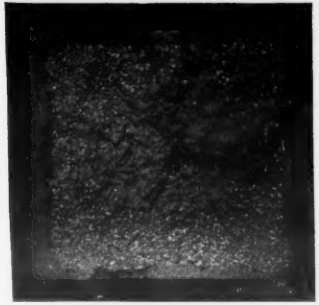


Fig. 12. Steel 5, heat 715°.

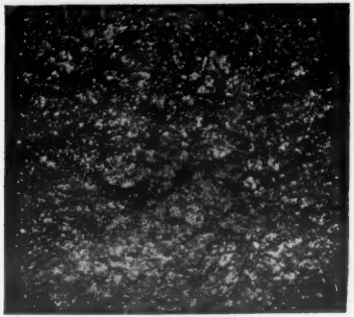


Fig. 13. Steel 5, heat 1070°.

Fig. 17. 1/2

Fig. 18. 1/2

Fig. 19. 1/2

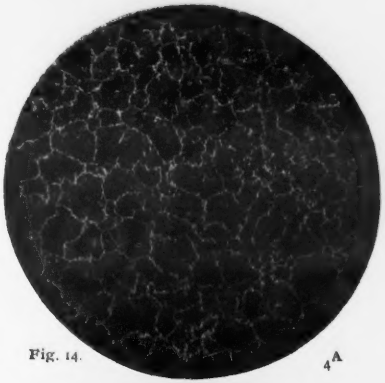


Fig. 14. 4^{A}

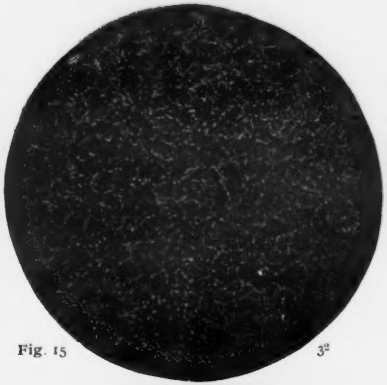


Fig. 15 3^{a}

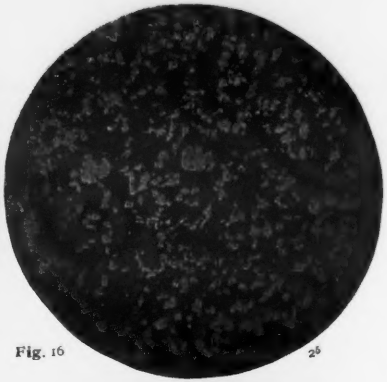


Fig. 16 2^{b}

Fig. 17. 1^{Z}

Fig. 18. 1^{a}

Fig. 19. 2^{a}

Fig. 23. 2°

Fig. 25. 4°

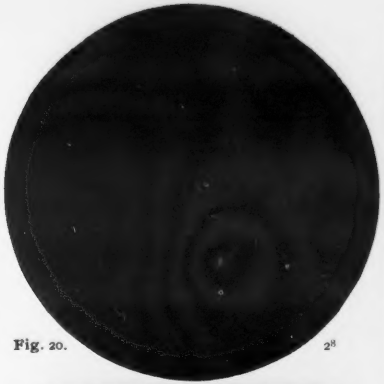


Fig. 20. 2ª

Fig. 21. 1ª

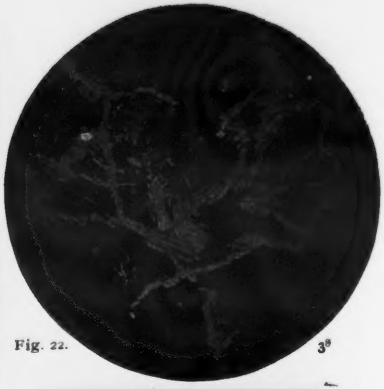


Fig. 22. 3ª

Fig. 23. 3ª

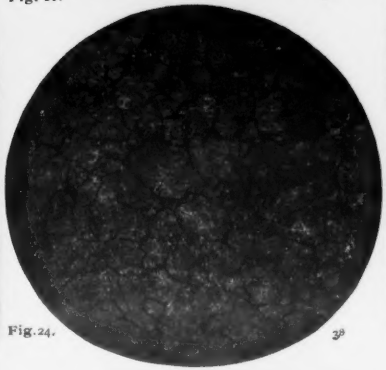


Fig. 24. 3ª

Fig. 25. 4ª

perature, 1200°, the maximum load takes a sudden drop and we have great overheating. The ductility on the other hand shows a steady fall to almost nil. An examination of the fractures shows a steady increase in size of grain up to 1070° at which point they suddenly become exceedingly coarse and show graphite. The microstructure shows a steady increase in the size of grains of the pearlite and of the segregation of the cementite. At the 1070° heat we see the breaking down of the segregated cementite into ferrite and graphite, with a great coarsening of the pearlite. In steels Nos. 3 and 4 the maximum heat, 1200°, produces another change, whereby the whole of the cementite is taken into solution resulting in a coarse network of cementite round large grains of pearlite. Such a structure accounts for the falling off in strength and ductility, while in the case of steels Nos. 1 and 2 this fall is apparently due to extreme coarseness of grain.

In the case of the steels low in carbon heating to temperatures above the critical point increases the strength compared with that of the refined bars. On the other hand, the ductility falls off. The fractures show that a temperature of 855° overheated steel No. 5, while 800° overheated steel No. 6, both of which are comparatively low temperatures. The microstructure shows that the pearlite has become coarse in grain and texture at these points, but it hardly accounts for the marked overheating at so low a temperature.

Thus we see that for each change in microstructure there is a corresponding change in mechanical properties and in fracture. So close are these relations that with little practice the latter can be predicted with certainty from the former.

Conclusion.—The above work is preliminary to a study of another series of six high carbon steels ranging in equal steps from 1 to 2 per cent. carbon and of larger cross-section, whereby it is hoped to work out definitely the change in steel of cementite = ferrite + graphite.

In conclusion I wish to acknowledge my indebtedness to the Carnegie Institution of Washington for a grant to carry on the work. I have also to thank Professor Howe and other friends for encouragement and advice.

LIST OF ILLUSTRATIONS.

Fig. 1.—Assembled fractures of test-pieces.
Figs. 2 to 13.—Fractures × 6 diameters.
Fig. 2.—Steel 2. C = 1.94 per cent. Heat 0. 905° C.
Fig. 3.— " 2. C = 1.94 " " 5. 950° C.
Fig. 4.— " 2. C = 1.94 " " Z. 1070° C.
Fig. 5.— " 2. C = 1.94 " " 8. 1200° C.
Fig. 6.— " 3. C = 1.72 " As rolled.
Fig. 7.— " 3. C = 1.72 " Heat 1. 715° C.
Fig. 8.— " 3. C = 1.72 " " Z. 1070° C.
Fig. 9.— " 3. C = 1.72 " " 8. 1200° C.
Fig. 10.— " 5. C = 1.04 " As rolled.
Fig. 11.— " 5. C = 1.04 " Heat 6. 650° C.
Fig. 12.— " 5. C = 1.04 " " 1. 715° C.
Fig. 13.— " 5. C = 1.04 " " Z. 1070° C.
Fig. 14.—25.—Microstructure.
Fig. 14.— " 4. C = 1.61 " As rolled × 260.
Fig. 15.— " 3. C = 1.72 " Heat 2. 800° C. × 260.
Fig. 16.— " 2. C = 1.94 " " 5. 950° C. × 260.
Fig. 17.— " 1. C = 2.04 " " Z. 1070° C. Corner × 44.
Fig. 18.— " 1. C = 2.04 " " 8. 1200° C. Center × 260.
Fig. 19.— " 2. C = 1.94 " " 8. 1200° C. Between center and outside × 200.
Fig. 20.— " 2. C = 1.94 " " 8. 1200° C. Near center of side × 60.
Fig. 21.— " 1. C = 2.04 " " 8. 1200° C. Between center and outside × 44.
Fig. 22.— " 3. C = 1.72 " " 8. 1200° C. Near outside × 260.
Fig. 23.— " 3. C = 1.72 " " 8. 1200° C. Center × 44.
Fig. 24.—The same, oblique illumination.
Fig. 25.—Steel 4. C = 1.61 per cent. Heat 8. 1200° C. Near center × 44.

METALLOGRAPHIC LABORATORY,
DEPT. OF METALLURGY,
COLUMBIA UNIVERSITY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

A REVISION OF THE ATOMIC WEIGHT OF BROMINE.

BY GREGORY PAUL BAXTER.

Received July 20, 1906.

IN numerous investigations in this laboratory upon the atomic weights of certain metals, in which metallic bromides were first titrated against the purest silver, and then the precipitated silver bromide was collected and weighed, the relation between the silver used in the titrations and the silver bromide obtained has yielded

data from which the atomic weight of bromine may be calculated. Furthermore, in all these investigations, as a check upon the purity of the silver and bromine employed, silver bromide was synthesized directly from weighed quantities of silver and an excess of ammonium bromide or hydrobromic acid. Many of these results have already been collected and discussed by Richards;[1] nevertheless they are cited in the following table together with a few more recent determinations.

INDIRECT DETERMINATIONS.

	Bromide analyzed.	Number of experiments.	Analyst.	Reference.	Ratio $\frac{Ag}{AgBr}$
1	$BaBr_2$	Last seven	Richards	Pr. Am. Acad., 28, 28	57.444
2	$SrBr_2$	Seven	"	Ibid., 30, 389	57.444
3	$ZnBr_2$	One	"	Ibid., 31, 178	57.445
4	$NiBr_2$	Seven	Cushman	Ibid., 33, 111	57.444
5	$CoBr_2$	Last five	Baxter	Ibid., 33, 127	57.446
6	UBr_4	Three	Merigold	Ibid., 37, 393	57.447
7	CsBr	Three	Archibald	Ibid., 38, 466	57.444
8	$FeBr_2$	Two	Baxter	Ibid., 39, 252	57.443
9	$CdBr_2$	Eight	Hines	This Journal, 28, 783	57.444
10	$MnBr_2$	Thirteen	"	Not yet published	57.444
	Average, weighted according to the number of determinations,				57.4443

DIRECT DETERMINATIONS.

11	HBr	Two	Richards	Pr. Am. Acad., 28, 17, 18	57.445
12	NH_4Br	One	"	Ibid., 30, 380	57.446
13	HBr	Two	"	Ibid., 31, 165	57.444
14	NH_4Br	One	Cushman	Ibid., 33, 106	57.445
15	NH_4Br	One	Baxter	Ibid., 33, 122	57.444
16	NH_4Br	Two	"	Ibid., 34, 353	57.447
17	NH_4Br	Three	"	Ibid., 39, 250	57.444
18	NH_4Br	One	Hines	Not yet published	57.443
	Average, weighted according to the number of determinations,				57.4447

From the first of these ratios the atomic weight of bromine, referred to silver 107.930, is found to be 79.956, and from the second 79.955.

Very recently, in experiments in which silver iodide was heated first in a current of air and bromine until the iodine was completely displaced, and then in a current of chlorine to displace the bromine, the ratio of silver bromide to silver chloride was determined in six cases. From the results of these experiments the atomic weight of bromine was calculated to be 79.953,[2] if the

[1] Pr. Am. Phil. Soc. 43, 119 (1904).

[2] Baxter: This Journal, 27, 884 (1905).

atomic weight of chlorine is assumed to be 35.473.[1]

These values for bromine are in close agreement with those of Stas.[2] In his experiments weighed quantities of pure silver and bromine were first titrated against each other, and then the precipitate of silver bromide was collected and weighed. Of the four results by the first method, one should be rejected according to his own statements, since the bromine was not thoroughly dried. The remaining three, 79.959, 79.961 and 79.960, give as an average 79.960. From the weight of silver bromide four values were obtained, 79.950, 79.952, 79.955 and 79.957, with an average of 79.954.

Marignac[3] also determined the ratio of silver to silver bromide, with somewhat lower results—79.959, 79.941 and 79.952; average, 79.950.

Scott,[4] in his analyses of ammonium bromide, obtained six values for the same ratio, varying between 79.936 and 79.948, with an average of 79.943. One of his results is here rejected, since the silver used in this experiment was known to be impure.

Dumas,[5] by heating silver bromide in chlorine, found the values 80.06, 79.89 and 79.96.

In computing the atomic weight of bromine from these data, great weight is always given to Stas's determinations, the value 79.955 being usually assumed as the most probable one for the constant in question. Certainly, as pointed out by Richards,[6] the true value must lie between 79.95 and 79.96. Clarke calculates the value 79.949 as the weighted average of the different investigations previous to Scott's.[7]

Considerable uncertainty exists as to the purity of the materials employed in much of the foregoing work. Richards and Wells[8] have already exhaustively investigated the various methods of preparing pure silver, and have found that while it is a comparatively simple matter to free this substance from metallic

[1] Richards and Wells: Publications of the Carnegie Institution, No. 28 (1905); This Journal, 27, 459.

[2] Œuvres Complètes, 1, 603.

[3] Ibid. 1, 81.

[4] J. Chem. Soc. 79, 147 (1901).

[5] Ann. Chem. Pharm. 113, 20 (1860).

[6] Pr. Am. Phil. Soc. 43, 119 (1904).

[7] "A Recalculation of Atomic Weights," Smith. Misc. Coll., 1897.

[8] Publications of the Carnegie Institution, No. 28, 16; also this Journal, 27, 472 (1905).

impurities, the absence of gaseous impurities is by no means so easy to secure. Oxygen may be eliminated best by fusion in an atmosphere of pure hydrogen gas,[1] or by prolonged fusion in a vacuum, while a lime boat was found to be the most suitable support for the silver during fusion.

In most of the experiments cited on page 202, one of the final steps in the purification of the silver was fusion of electrolytic crystals on lime, in many cases in a vacuum, but without especial care to prolong the fusion. Silver prepared in this way was found by Richards and Wells to contain traces of oxygen, derived from silver nitrate occluded by the electrolytic crystals. In cases 8, 9, 10, 17 and 18, however, the silver was fused in hydrogen. Richards and Wells showed also that Stas's silver contained at least 0.01 per cent. of impurity, since it yielded 0.01 per cent. less silver chloride than their purest silver.[2] Scott's silver in three cases was merely heated, not fused, in hydrogen, and in two of the others was fused before a blowpipe on calcium phosphate. In one experiment only the metal was fused on lime. No details are given as to the purification of the silver used by Marignac.

Bromine also may be freed from impurities only with some difficulty. Experience in this laboratory has shown that chlorine may be eliminated most conveniently by distilling or precipitating the bromine from solution in a bromide. One such distillation is sufficient to remove chlorine completely only when the substance is initially comparatively pure. If, however, the process is repeated by converting a portion of the partially purified product into a bromide, and dissolving the remainder of the bromine in this comparatively pure bromide, the chlorine is eliminated so completely that further repetitions of this process have no apparent effect.[3] The removal of iodine may be easily effected by converting the bromine into hydrobromic acid or a soluble bromide, and boiling the solution with a small quantity of free bromine. Here again it is well to repeat the process several times, since the reaction between free bromine and the iodine ion, like that between free chlorine and the bromine ion, is undoubtedly incomplete.

[1] Baxter: Pr. Am. Acad. Arts Sci. 39, 249 (1903).

[2] Loc. cit., page 62.

[3] Attention has already been called to these points by Richards and Wells: Pr. Am. Acad. Arts Sci., 41, 440 (1906).

The greater part of the experiments cited on page 1323 were made with bromine which had been purified with due observance of these precautions. Of the other investigators, Stas seems to have been the only one to use sufficient pains to secure purity of the bromine. Stas removed iodine by shaking potassium bromide several times with free bromine and carbon disulphide, and in the course of the prolonged purification distilled the bromine twice from solution in a bromide. Marignac's purification consisted solely in crystallization of barium bromate and Scott's in distillation of hydrobromic acid.

Of the methods employed in these early determinations, that involving the analysis of metallic halides is least suited for the purpose, on account of the danger of occlusion of metallic salts by the precipitated silver bromide. That such an error actually exists to a slight extent is shown by the fact that the average of the "indirect" determinations is slightly larger than the average of the "direct" determinations. Obviously, if silver bromide is precipitated by means of either ammonium bromide or hydrobromic acid, occluded ammonium salts or free acids could be easily expelled by fusion of the bromide. This precaution was observed in most of the determinations recorded on page 202, and is absolutely essential for the complete elimination of water from the salt. Stas and Marignac both fused the silver bromide in their syntheses, but this precaution was omitted by Scott, who dried the bromide at 180°. Scott's statement that the loss on fusion of silver bromide which had been dried at 180° was due to the presence of asbestos is contradicted by the experiments recorded later in this paper, in which the loss on fusion amounted to about 0.01 per cent. in the case of silver bromide which had been dried in a similar fashion and which was almost entirely free from asbestos.

From this brief discussion of the more important errors which may have influenced previous determinations of the atomic weight of bromine, it is evident that some uncertainty still exists as to the true value of this constant. In the hope of throwing new light upon the subject, experiments were carried out by two of the methods outlined above, with especial precautions to insure purity of materials and to eliminate known possible errors in the experimental methods.

Both the methods chosen—synthesis of silver bromide from a weighed amount of silver, and conversion of silver bromide into

silver chloride—have already been recently tested in this laboratory,[1] and have been found to be at least as satisfactory as any.

PURIFICATION OF MATERIALS.

Bromine.—In purifying bromine for this research, the principles set forth on page 1325 of this paper were applied, but in some cases the purifying processes were repeated after the product was apparently pure, in order to make certain that further treatment had no effect.

Sample I was first completely dissolved in calcium bromide which had been made from about one-third of the original material by means of lime and ammonia, and was then distilled from the solution. The product was covered with several times its volume of water, and was converted into hydrobromic acid by means of pure hydrogen sulphide which had been generated from ferrous sulphide with dilute sulphuric acid, and which had been thoroughly washed with water. After filtration from the precipitated sulphur and bromide of sulphur, the acid was boiled for some time, with occasional addition of small quantities of recrystallized potassium permanganate to eliminate the iodine. Finally, the residual hydrobromic acid was heated with an equivalent amount of recrystallized permanganate, and the bromine was condensed in a flask cooled with ice.

Sample II was first converted into hydrobromic acid by means of red phosphorus and water, and the hydrobromic acid was then distilled, after having been boiled with an excess of bromine. An equivalent amount of permanganate was added, and the bromine liberated was separated from the solution by distillation. About one-fourth of the product was next transformed into calcium bromide by means of ammonia and lime which was free from chloride, and the remaining three-fourths of the bromine were dissolved in the calcium bromide and distilled. Still a third distillation from a bromide was carried out by reducing the product of the second distillation with hydrogen sulphide and subsequently oxidizing the hydrobromic acid with the purest recrystallized potassium permanganate, after boiling the acid with several small portions of permanganate to eliminate the last traces of iodine.

Sample III was obtained by preparing calcium bromide from a

[1] Baxter: Pr. Am. Acad. Arts Sci. 40, 419; 41, 73. Richards and Wells: Publications of the Carnegie Institution, No. 28; This Journal, 27, 876 (1905).

portion of Sample II and distilling the remainder of Sample II from solution in this bromide.

In the case of Sample IV the processes of reduction to hydrobromic acid with hydrogen sulphide and oxidation of the hydrobromic acid with pure permanganate were four times repeated. After each reduction the hydrobromic acid was boiled with free bromine to remove iodine.

Sample V was three times reduced with hydrogen sulphide and oxidized with permanganate. One-fourth the product was converted into calcium bromide and the remainder was dissolved in this calcium bromide and distilled.

Thus Sample I was twice distilled from a bromide; Sample II was treated three times in the same way; and Samples III, IV and V four times.

Shortly before use each sample was distilled and converted into ammonium bromide by slow addition to an excess of redistilled ammonium hydroxide. The solution was then boiled to expel the excess of ammonia.

Silver.—Several different samples of silver were employed, many of which have already been used in atomic weight researches in this laboratory, and have shown evidence of great purity. For details concerning the purification the papers referred to should be consulted.

Sample A was employed in a determination of the atomic weight of iodine.[1] This specimen had been twice precipitated as chloride and once electrolyzed.

Sample B was used in experiments upon the atomic weight of iodine[2] and of manganese.[3] It was precipitated once as chloride, electrolyzed once, and finally precipitated as metal with ammonium formate.

Sample C also was employed in a determination of the atomic weight of manganese, and was purified by recrystallizing silver nitrate, seven times from nitric acid and five times from aqueous solution. Finally, the silver nitrate was reduced by means of ammonium formate.

Sample D was prepared for the determination of the atomic

[1] Baxter: Pr. Am. Acad. Arts Sci. 40, 420 (1904); This Journal, 27, 881 (1905).

[2] Baxter: Pr. Am. Acad. Arts Sci. 41, 79 (1905); This Journal, 27, 881 (1905).

[3] Baxter and Hines: This paper will soon be published.

weights of cadmium[1] and manganese, by one precipitation as chloride, one precipitation with ammonium formate, and one electrolysis.

Sample E was first purified in part by precipitation as chloride, in part by precipitation with ammonium formate. The combined material was then subjected to two electrolyses.

In all cases the electrolytic crystals were fused in a boat of the purest lime, contained in a porcelain tube, in a current of electrolytic hydrogen. After the buttons had been cleansed with dilute nitric acid and dried at 200°, they were cut into fragments of from 4 to 8 grams either by means of a clean chisel and anvil or with a fine jeweler's saw. The latter method was employed in the case of Samples D and E, because it proved easier completely to free the silver from surface contamination with iron by etching the fragments with nitric acid, than when a chisel was used. The cleansing process with nitric acid was repeated until the solution thus obtained, after precipitation with hydrochloric acid and evaporation, proved free from iron. That every trace of iron could be removed by this treatment was proved by testing for iron the evaporated filtrates from several of the analyses subsequently recorded in this paper. Negative results were obtained in all cases.

After thorough washing with water and drying at 100°, the pieces of metal were heated to about 400° in a vacuum, and were preserved over solid potassium hydroxide in a desiccator.

THE RATIO OF SILVER TO SILVER BROMIDE.

The ratio of silver to silver bromide was determined as follows: Weighed quantities of silver were dissolved in the purest redistilled nitric acid diluted with an equal volume of water, in a flask provided with a column of bulbs to catch possible spatterings. However, during the solution of the silver the temperature was kept so low that almost no gas was evolved, and hence there was very little danger from this source. Next the acid solution of the silver was diluted with an equal volume of water, and was heated until free from nitrous acid and oxides of nitrogen. After still further dilution, the solution was added slowly with constant agitation to a dilute solution of an excess of ammonium bromide in a glass-stoppered precipitating flask, and the whole was violently

[1] Baxter and Hines : This Journal, 28, 772 (1906).

shaken for some time to promote coagulation. By adding the silver solution to the bromide, occlusion of silver nitrate was almost wholly precluded. In some experiments the solutions were as dilute as twentieth-normal, in others as concentrated as fourth-normal. The final results seemed to be independent of the concentration of the solutions. At the end of about twenty-four hours the flask with its contents was again shaken, and then it was allowed to stand until the supernatant liquid was perfectly clear. The precipitate of silver bromide was collected upon a weighed Gooch crucible, after thorough washing by decantation with water, and was dried in an electric oven, first for several hours at 130°, finally for about fourteen hours at 180°. Then it was cooled and weighed.

The operations of precipitation and filtration were performed in a large cupboard lighted with red light, and if the flask was taken out of this cupboard it was enveloped in several thicknesses of black cloth.

Even after the prolonged drying, traces of moisture were retained by the salt, and could be expelled only by fusion. This was done by transferring the bulk of the silver bromide, freed as completely as possible from asbestos, to a small porcelain crucible which was weighed with its cover. The silver bromide was then fused by heating the small crucible, contained in a large crucible to prevent direct contact with the flame of the burner. A temperature much above the fusing point of silver bromide was avoided so that volatilization of the salt could not take place. This treatment must have eliminated occluded ammonium salts as well as water. Finally, in order to convert any occluded silver nitrate, metallic silver, or silver sub-bromide into silver bromide, the salt was again fused in a current of dry air containing bromine vapor. This treatment seldom produced any measurable effect either upon the weight or the appearance of the salt, which was perfectly transparent and of a light yellow color even after the first fusion in air.

A few shreds of asbestos displaced from the crucible, together with an occasional trace of silver bromide which escaped the crucible, were collected upon a tiny filter-paper which was then ignited in a porcelain crucible. Before being weighed the ash was either treated with a drop of nitric and hydrobromic acids

and again heated, or else was heated for some minutes in a current of air and bromine.

The filtrate and washings were evaporated to small bulk. The precipitating flask and all other glass vessels used in the analysis were rinsed with ammonia and the rinsings were added to the evaporated filtrate and wash-waters. The whole was then tested in a nephelometer for silver and the quantity found was estimated by comparison with standard silver solutions. In most cases the correction thus obtained was less than 0.1 mg.

The asbestos which formed the felt in the Gooch crucible, after having been shredded, was digested for some hours with aqua regia and was then thoroughly washed with water. Before the empty crucible was weighed, the felt was ignited with a Bunsen burner. Crucibles thus treated and then heated to 180° after being moistened with water did not change in weight.

In the following table are cited all the analyses which were completed without accident. Vacuum corrections of —0.000031 for every apparent gram of silver and of +0.000041 for every apparent gram of silver bromide are applied.[1] The atomic weight of silver is assumed to be 107.930.

The platinum plated brass weights were standardized from time to time and were found to retain their original values within a very few hundredths of a milligram in all cases.

THE RATIO OF SILVER BROMIDE TO SILVER CHLORIDE.

The ratio of silver bromide to silver chloride was determined much as described in previous papers upon the atomic weight of iodine.[2] Pure silver bromide was prepared by precipitation of silver nitrate with an excess of ammonium bromide. The silver employed was purified either by precipitation as chloride and reduction with invert sugar, or by electrolysis, or by precipitation with ammonium formate. The metal was then fused before a blowpipe upon a crucible of the purest lime, and the buttons were thoroughly cleansed with nitric acid. No further purifica-

[1] The specific gravity of the weights was determined to be 8.3. The specific gravity of silver has been found to be 10.49. Richards and Wells: Publications of the Carnegie Institution, No. 28, 11. The specific gravity of fused silver bromide has been found to be 6.473. Baxter and Hines: Am. Ch. J. 31, 224.

[2] Baxter: Pr. Am. Acad. Arts Sci. 40, 432 (1904); 41, 75 (1905); This Journal, 27, 876 (1905).

TABLE I.—THE ATOMIC WEIGHT OF BROMINE. SERIES I.

Ag : AgBr. Ag = 107.930

Number of analysis.	Sample of silver.	Sample of bromine.	Weight of silver in vacuum. Grams.	Weight of silver bromide in vacuum. Grams.	Loss on fusion in bromine. Grams.	Weight of asbestos. Grams.	Dissolved silver bromide. Grams.	Corrected wt. of silver bromide. Grams.	Ag / AgBr. Ratio	Atomic weight of bromine.
1	A	II	4.71853	8.21362	0.00027	0.00007	0.00021	8.21363	57.4476	79.946
2	B	II	5.01725	8.73387	0.00020	0.00019	0.00007	8.73393	57.4455	79.952
3	A	II	5.96818	10.38799	0.00023	0.00034	0.00122	10.38932	57.4453	79.953
4	C	II	5.62992	9.80000	0.00017	0.00039	0.00017	9.80039	57.4459	79.951
								Average,	57.4461	79.950
5	A	IV	8.13612	14.16265	0.00002	0.00047	0.00024	14.16334	57.4449	79.954
6	C	IV	5.07238	8.82932	0.00013	0.00043	0.00035	8.82997	57.4451	79.954
7	B	IV	4.80711	8.36838	0.00015[1]	0.00000	0.00004	8.36827	57.4445	79.956
								Average,	57.4448	79.955
8	C	V	4.27279	7.43771	0.00010[1]	0.00009	0.00007	7.43776	57.4473	79.947
9	A	V	5.86115	10.20299	0.00007[1]	0.00004	0.00003	10.20299	57.4454	79.953
10	B	V	7.91425	13.77735	0.00010	0.00010	0.00001	13.77736	57.4439	79.958
11	D	V	6.40765	11.15461	0.00000	0.00006	0.00001	11.15468	57.4436	79.959
12	D	V	6.38180	11.10942	0.00025	0.00012	0.00001	11.10930	57.4456	79.952
13	D	V	6.23696	10.85722	0.00005	0.00004	0.00001	10.85722	57.4453	79.953
								Average,	57.4452	79.953
14	E	I	9.18778	15.99383	0.00014	0.00019	0.00004	15.99392	57.4455	79.953
15	E	I	8.01261	13.94828	0.00018	0.00009	0.00007	13.94826	57.4452	79.953
16	E	I	10.48638	18.25467	0.00025[1]	0.00007	0.00001	18.25452	57.4454	79.953
								Average,	57.4454	79.953
17	E	III	8.59260	14.95790	0.00014	0.00016	0.00005	14.95797	57.4450	79.954
18	E	III	8.97307	15.62013	0.00004	0.00007	0.00006	15.62022	57.4452	79.953
								Average,	57.4451	79.954
		Total,	121.67653					211.81305	57.4452	79.953
								Average of all 18 determinations,	57.4453	79.953
								Average of last 7 determinations,	57.4453	79.953

[1] Fusion in bromine lost, after the salt had been fused in air.

tion was considered necessary, since the weight of the metal was of no consequence.

After the silver bromide had been washed by decantation with water, in some cases it was collected in a Gooch crucible in which a disk of filter-paper was employed instead of asbestos, and after drying at 100° it was carefully separated from the filter-paper. In other cases the precipitate was transferred to a platinum dish, and was drained with a platinum reverse filter[1] with a disk of filter-paper. In still others a platinum Gooch crucible with small holes was found to be sufficiently effective as a filtering medium without the use of either asbestos or filter-paper.

Before being weighed the silver bromide was fused in a current of air saturated with bromine in a weighed quartz crucible. The air was purified by passing successively over beads moistened with silver nitrate solution, over sodium carbonate, and finally over concentrated sulphuric acid which had been heated to its boiling-point with a small quantity of recrystallized potassium dichromate to eliminate volatile and oxidizable impurities. The air was then passed through dry bromine in a small bulb. This apparatus was constructed entirely of glass with ground joints. The tube which conducted the gases into the crucible passed through a Rose crucible cover of glazed porcelain in all experiments except analyses 28 to 31, in which a quartz cover was employed. The quartz crucibles were always contained in large porcelain crucibles while being heated. They remained almost absolutely constant in weight during the experiments. The bromine was in each case a portion of the sample from which the silver bromide had been made.

Next the bromide was heated barely to fusion in a slow current of chlorine, generated by the action of hydrochloric acid upon manganese dioxide, and dried by means of concentrated sulphuric acid. The apparatus for this purpose also was constructed wholly of glass. When the bromine was apparently completely displaced, the silver chloride was heated in the air for a few minutes to expel dissolved chlorine, and then was cooled and weighed. A repetition of the heating in chlorine seldom affected the weight of the salt more than a few hundredths of a milligram, although occasionally a third heating was necessary to effect this result.

That no loss of silver chloride by volatilization took place is

[1] Cooke: Pr. Am. Acad. Arts Sci. 12, 121.

certain for two reasons. In the first place the cover of the crucible and the delivery tube for the bromine when rinsed with ammonia and the solution treated with a slight excess of hydrochloric acid gave no visible opalescence in the nephelometer. In the second place the weight of the chloride became constant without difficulty. It has already been shown that silver chloride which has been fused in chlorine, if subsequently heated in air, retains no excess of chlorine.[1]

The following vacuum corrections were applied: Silver bromide, +0.000041; silver chloride, +0.000071.[2] The atomic weight of chlorine referred to silver 107.930 is assumed to be 35.473.

Aside from the close agreement of all the results of Series I, the fact is to be emphasized that of the last seven analyses, which were consecutive, only two differ from the average of the series, 79.953, by as much as one one-thousandth of a unit. Furthermore, there is no evidence of any dissimilarity in the different preparations of bromine. Material which has received only two distillations from a bromide gives values no lower than bromine which has been thus treated four times. The various specimens of silver also show no difference in purity.

In the case of Series II, the extreme variation of the results is only four-thousandths of a unit, and only one of the thirteen experiments yielded a value which differs from the average by more than one one-thousandth of a unit.

Finally, the difference between the averages of Series I and II is only seven ten-thousandths of a unit. It is extremely unlikely that constant errors could have affected both series equally, so that this striking agreement is strong proof that both series are free from such errors.

It has already been pointed out that the average of Stas's syntheses, 79.954, probably represents with considerable accuracy the atomic weight of bromine, and that certainly his determinations are more accurate than those of later experimenters. His syntheses are few in number, however, and differ among themselves by several thousandths of a unit, so that they do not define within this amount the constant in question. Their average,

[1] Baxter: Pr. Am. Acad. Arts Sci. 40, 432 (1904); This Journal, 26, 1591 (1904); Richards and Wells: Publications of the Carnegie Institution, No. 28, page 59.

[2] Richards and Stull have found the density of fused silver chloride to be 5.56.

however, confirms the value obtained in this paper. From all the experiments here described the number 79.953 seems to be the most probable value for the atomic weight of bromine if the atomic weight of silver is assumed to be 107.930.

TABLE II.—THE ATOMIC WEIGHT OF BROMINE. SERIES II.

AgBr : AgCl.

Ag = 107.930 Cl = 35.473.

Number of analysis.	Sample of bromine.	Weight of silver bromide in vacuum. Grams.	Weight of silver chloride in vacuum. Grams.	Ratio AgBr/AgCl.	Atomic weight of bromine.
19	II	8.03979	6.13642	131.0176	79.953
20	II	8.57738	6.54677	131.0170	79.952
21	II	13.15698	10.04221	131.0168	79.952
			Average,	131.0171	79.952
22	IV	12.71403	9.70413	131.0167	79.952
23	IV	13.96784	10.66116	131.0162	79.951
			Average,	131.0164	78.952
24	V	13.08168	9.98469	131.0174	76.953
25	V	12.52604	9.56059	131.0175	79.953
26	V	11.11984	8.48733	131.0170	79.952
27	V	8.82272	6.73402	131.0172	79.953
			Average,	131.0173	79.953
28	I	11.93192	9.10721	131.0162	79.951
29	I	12.53547	9.56767	131.0190	79.955
			Average,	131.0176	79.953
30	III	17.15021	13.09009	131.0167	79.952
31	III	10.31852	7.87572	131.0168	79.952
			Average,	131.0168	79.952
	Total,	153.94242	117.49801	131.0170	79.952
			Average of all 13 experiments,	131.0171	79.952
			Average of Series I and II,		79.953

In conclusion, attention may be called to the fact that a diminution in the atomic weight of bromine raises slightly all atomic weights resulting from the analysis of metallic bromides by precipitation with silver.

I am deeply indebted to the Carnegie Institution of Washington and to the Cyrus M. Warren Fund for Research in Harvard University for assistance in pursuing this investigation.

CAMBRIDGE, MASS.

[Contributions from the Chemical Laboratory of Harvard College.]

THE SOLUBILITY OF POTASSIUM PERMANGANATE.

By Gregory P. Baxter, Arthur C. Boylston and Robert A. Hubbard.

Received July 26, 1906.

Determinations of the solubility in water of potassium permanganate have been made by Mitscherlich,[1] who found 6.3 parts of salt to 100 parts of water in a saturated solution at 15°, by Guthrie,[2] who found 2.9 parts of salt to 100 parts of water at —0.6°, and by Muthmann and Kuntz,[3] who found 41.81 grams of permanganate dissolved in 1 liter of water at "about 7°." The data obtained in the present investigation cover the above range of temperature and extend as high as 65°.

Potassium permanganate for the determinations was purified by crystallization. The salt was first dissolved in the purest water and the solution was filtered through asbestos in a Gooch crucible without being allowed to come in contact with rubber. The solution was then evaporated in covered flasks to crystallization and the product was twice recrystallized, with centrifugal drainage. In all three crystallizations the hot solution was allowed to stand some time and was carefully decanted from possible sediment before cooling. All the water used in the purification and also in the analyses of the saturated solutions was twice distilled, once from an alkaline solution of permanganate and once from a trace of sulphuric acid. The final product, when dissolved in the purest water, did not appreciably stain clean glass, and showed every outward evidence of purity.

The method of obtaining a saturated solution was the usual one of rotating the substance with water in closed tubes at the desired temperature in a thermostat. By means of electrical regulating apparatus the thermostat was maintained constant at different temperatures to within five hundredths of a degree. The thermometer was carefully corrected by comparison with one standardized by the Physikalisch-technische Reichsanstalt.

Since permanganates are easily reduced by rubber or cork, and since glass stoppers may become loose or may leak, the glass tubes,

[1] Pogg. Ann. **25**, 295 (1832).

[2] Phil. Mag. [5] **6**, 37 (1878).

[3] Z. Krist. Min. **23**, 374 (1894).

2 cm. in diameter, in which the solutions were shaken, were sealed off after the permanganate and water had been introduced.

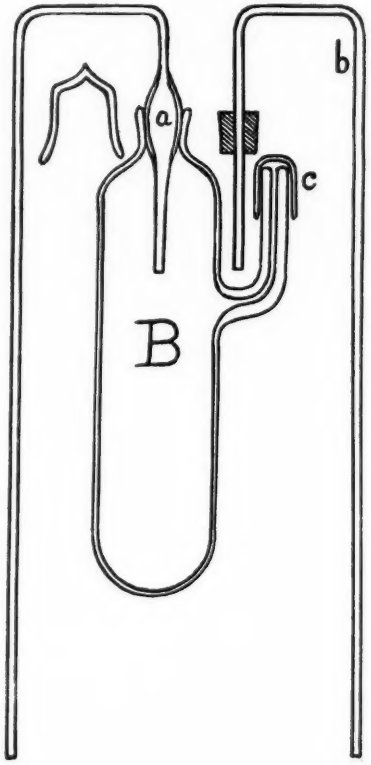
It was found advisable to rotate the tubes for at least four hours although in a few cases the saturation equilibrium was reached in a shorter period. In some experiments the agitation was continued for more than twenty hours but the results in these cases were essentially the same as in those where the solutions were analyzed after four hours' shaking. It was necessary to shake the solutions quite as long at the higher temperatures as at the lower.

After saturation had been attained, the tubes were allowed to stand in a perpendicular position in the thermostat for from two to four hours in order to allow all solid matter to settle. The dark color of the permanganate made it impossible to see whether the solution was absolutely free from small suspended particles of salt, and the nature of the permanganate made it inadvisable to attempt filtration of the solutions. However, since solutions after only two hours' standing showed the same salt content as similar solutions which had settled for four hours, it seems probable that no error was introduced from this source.

For removing the solution from the saturating tubes a pipette of the following form was used. A capillary tube with an enlargement at *a* was ground into the mouth of the bulb *B*. The pipette was filled by cutting off the top of the sealed saturating tube without removing it from the thermostat, inserting the capillary tube *a* into the saturated solution, and applying suction at *c*. *a* was then removed and both the mouth of the bulb *B* and the capillary side-tube were covered with glass caps. The bulb was wiped with a damp cloth, and, after it had been allowed to come to constancy in the balance case, was weighed. Evaporation from one of these pipettes was very slow. A solution at about 20°, on standing in a balance case containing sulphuric acid, lost only 3 mg. in fifteen hours. Since at higher temperatures the danger of evaporation is increased, the solutions were cooled with ice water as soon as they were removed from the saturating tubes.

With solutions saturated at the higher temperatures it was found necessary to warm the capillary tubes before pipetting out the solution, in order to avoid the deposition of crystals in the

enlargement *a*, although no salt deposited in the capillary itself. Capillary tubes of the form *b*, without an enlargement, were also used. These tubes were fitted into the bulb by means of a rubber stopper. The results with these tubes were no different from those obtained by warming the tubes of the form *a*.



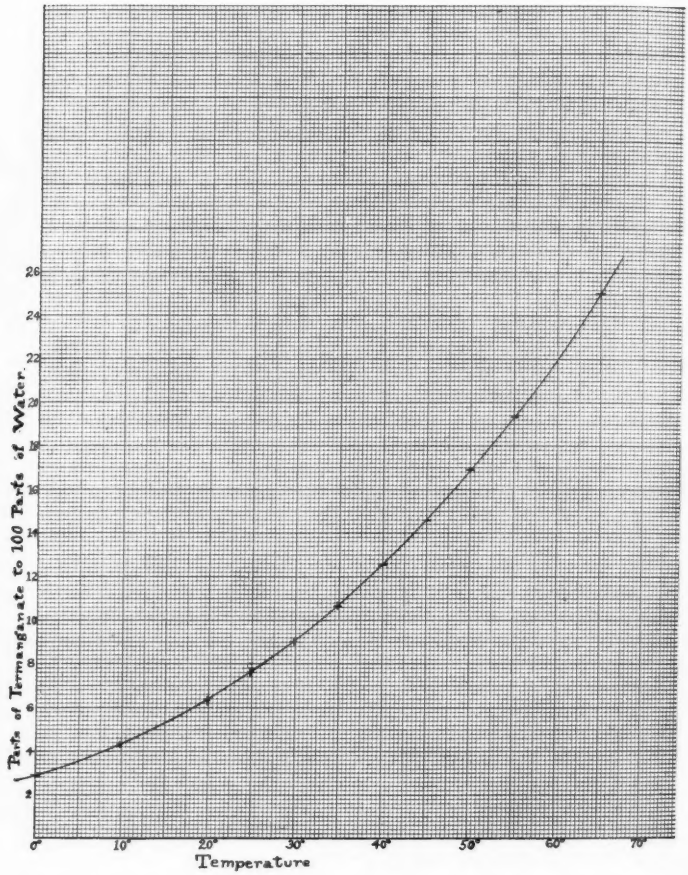
In order to make certain that saturation had been reached from below, the equilibrium was approached also from above. This was done by agitating the solution for an hour or two at a temperature from 5° to 10° above the temperature in question, and continuing the agitating at the desired temperature for from four to twenty hours. Experiments by this method gave pre-

cisely the same results as those where equilibrium was reached from the other direction.

Three methods of analyzing the saturated solutions were employed. The simplest and least satisfactory was that of evaporating weighed portions of the solutions to dryness in platinum crucibles and heating the residues to 150° in an air-bath. During the evaporation evidence of slight reduction of the permanganate always appeared. On the other hand it is improbable that all the water was expelled at 150°. A temperature much higher than this was found to produce considerable reduction of the salt. However, the two errors mentioned above would affect the results in opposite directions.

The second method of determining the permanganate was to weigh the potassium and manganous sulphates formed by reduction of the permanganate with sulphurous acid. The permanganate, after being weighed, was transferred to a platinum dish and was treated with a slight excess of sulphurous acid. The solution was then evaporated upon the steam-bath, first in the dish, then in a weighed platinum crucible. Finally the greater part of the excess of sulphuric acid was expelled upon a ring-burner and the last traces were eliminated by prolonged heating over a small Bunsen flame. Much care during the final heating was necessary to avoid partial decomposition of the manganous sulphate, with the formation of manganic oxide. It was possible, however, to obtain a product that gave a perfectly clear solution in water, showing that no decomposition had taken place, and which nevertheless was not acid to methyl orange. The sulphurous acid was made from concentrated sulphuric acid and copper, and was redistilled.

The third method of analysis was titration with oxalic acid. This acid was many times recrystallized, first from hydrochloric acid solution, then from water until free from chlorides. In order to bring it to the theoretical composition, it was finely powdered and exposed in a thin layer in a desiccator over sulphuric acid of the specific gravity 1.35. A slight deficiency of oxalic acid was weighed out and dissolved in water. Then, after the addition of a considerable excess of sulphuric acid, the permanganate was slowly introduced into the hot solution of oxalic and sulphuric acids. Finally the slight excess of permanganate was reduced by means of a fifth-normal oxalic acid solution. In a few cases



where the oxalic acid was in excess the end-point was reached by means of a standard solution of permanganate.

Since all three methods gave essentially identical results, it is highly probable that no constant errors affected any one of them to an appreciable extent.

In the following table the starred determinations were made with solutions which had been first supersaturated.

Temperature.	Period of shaking. Hours.	Weight of solution. Grams.	Weight of $KMnO_4$. Grams.	Weight of $K_2SO_4.2MnSO_4$. Grams.	Weight of $H_2C_2O_4.2H_2O$. Grams.	Per cent. of $KMnO_4$.
0°	4.5	12.489*		0.5190		2.759
	4.5	12.438			0.6838	2.758
	4.5	11.791		0.4902		2.760
	4.5	11.798			0.6461	2.747
	4.5	10.684*		0.4443		2.761
	4.5	9.686*			0.5297	2.743
	4.5	12.354*			0.6765	2.747
					Average,	2.754
9.8°	4	10.433*	0.4319			4.140
	4	8.924*			0.735	4.132
	4.5	10.098*	0.4176			4.136
	4.5	9.385*			0.772	4.127
	4	8.944*		0.5577		4.140
	4	9.340*			0.768	4.125
					Average,	4.133
19.8°	5	9.609	0.5737			5.970
	5	8.172			0.969	5.948
	18	10.624	0.6342			5.970
	18	10.624		0.9535		5.959
	18	9.012			1.066	5.934
	18	9.870		0.8879		5.973
	16	10.431*		0.9369		5.964
	16	8.870*			1.051	5.944
	16	10.480*			1.244	5.955
	16	9.051*	0.5394			5.960
					Average,	5.958
24.8°	4	11.368		1.2081		7.056
	4	11.018*		1.1716		7.060
	4	13.325*		1.4189		7.070
	5	11.301[1]		1.2000		7.050
	5	14.793[1]		1.5681		7.038
	5	13.686[1]		1.4569		7.068
	28	15.758[1]		1.6728		7.048
	23	12.191[1]		1.2963		7.060
	5	14.932*[1]		1.5820		7.035
	5	13.939*[1]		1.4826		7.062
					Average,	7.055

Temperature.	Period of shaking. Hours.	Weight of solution. Grams.	Weight of $KMnO_4$. Grams.	Weight of $K_2SO_4.2MnSO_4$. Grams.	Weight of $H_2C_2O_4 2H_2O$. Grams.	Per cent. of $KMnO_4$.
29.8°	4	9.141		1.1391		8.274
	4	9.804		1.2237		8.287
	4	9.021			1.491	8.292
	3	9.015*	0.7474			8.291
	3	9.015*		1.1239		8.278
	3	9.972*		1.2440		8.283
	20	8.803		1.0963		8.269
	20	9.857			1.628	8.286
					Average,	8.283
34.8°	4	8.170*			1.5700	9.640
	4	8.691*		1.2652		9.666
	4.5	8.986			1.723	9.619
	4.5	11.202	1.0815			9.655
	4.5	9.874			1.892	9.613
	4	13.749			2.638	9.625
	4	9.694		1.4066		9.634
	4	8.542*			1.644	9.655
	4	6.675*		0.9715		9.664
	4	8.916*			1.717	9.661
					Average,	9.643
40°	18	10.934			2.4286	11.143
	18	9.498			2.1134	11.163
	18	9.374		1 5740		11.149
	18	11.123		1.8617		11.113
	18	10.704			2.3809	11.159
	18	11.245			2.4996	11.151
	18	11.774*	1.3174			11.189
	18	10.063*			2.2414	11.174
					Average,	11.155
45°	4	10.562*			2.682	12.739
	4	11.403*			2.895	12.736
	4	9.812			2.486	12.710
					Average,	12.728
50°	20	11.499			3.3095	14.438
	20	10.965			3.1571	14.443
	20	10.455		2.2764		14.457
	20	9.794			2.817	14.429
	36	12.182*			3.508	14.446
	30	11.896*		2.5920		18.465
					Average,	14.446

Temperature.	Period of shaking. Hours.	Weight of solution. Grams.	Weight of $KMnO_4$. Grams.	Weight of $K_2SO_4.2MnSO_4$. Grams.	Weight of $H_2C_2O_4 2H_2O$. Grams.	Per cent. of $KMnO_4$.
55°	25	9.960			3.216	16.198
	25	9.995		2.4404		16.212
	25	8.675			2.802	16.203
	17	12.090*			3.904	16.199
	17	8.481*		2.0685		16.193
	17	8.675*			2.802	16.203
					Average,	16.201
65°	4	7.801		2.3531		20.028
	4	6.987			2.744	19.988
	4	9.049			3.607	19.994
	4	7.810*		2.3597		20.060
	4	6.763*		2.0382		20.010
	4	6.809*		2.0555		20.043
					Average,	20.021

Temperature. Degrees.	Per cent. of $KMnO_4$.	Parts of $KMnO_4$ to 100 parts of water.
0	2.75	2.83
9.8	4.13	4.31
19.8	5.96	6.34
24.8	7.06	7.59
29.8	8.28	9.03
34.8	9.64	10.67
40.0	11.16	12.56
45.0	12.73	14.58
50.0	14.45	16.89
55 0	16.20	19.33
65.0	20.02	25.03

CAMBRIDGE, MASS.,
July 24, 1906.

THE NITRIDES OF ZINC, ALUMINIUM AND IRON.

BY ALFRED H. WHITE AND L. KIRSCHBRAUN.

Received July 19, 1906.

THE action of ammonia at high temperatures upon metals has already been investigated by Beilby and Henderson[2] who showed that almost all metals are profoundly modified in their physical properties upon exposure to ammonia gas at a red heat. In their experiments nitrides of approximately definite composition were formed from some metals, but in more cases the percentage of

[1] These determinations were prepared by Mr. Hubbard, the remainder by Mr. Boylston.

[2] J. Chem. Soc. 79, 1245.

nitrogen fixed was small and variable, and frequently the only evidence that there had been combination between the nitrogen and metal was obtained from the porous structure after the operation.

We have studied the action of ammonia gas upon zinc, aluminium, and iron in as nearly a quantitative manner as possible and present here the results which are new. The apparatus and methods were in general the same as those previously employed by one of us in measuring the decomposition of ammonia at high temperatures.[1]

Zinc Nitride and the Action of Ammonia upon Zinc.—We have found no record in the literature of a previous study of this reaction. When ammonia was passed over granulated zinc at a temperature of 500° or below, no evidence of appreciable fixation of nitrogen could be detected on solution of the treated metal in acid. The most favorable temperature for the absorption of nitrogen seemed to be 600°, granulated zinc at this temperature taking up 2 per cent. of nitrogen in thirty minutes. The percentage absorbed was not increased by a longer stay in the furnace. Higher temperatures caused much volatilization of zinc without fixation of nitrogen. Sheet zinc at 600° gave only a trace of nitride. When ammonia was bubbled through molten zinc, fine particles were thrown up which stuck to the walls of the test-tube and contained as high as 3.7 per cent. of nitrogen. Zinc dust fixed a larger amount of nitrogen and the resulting product contained as much as 10.6 per cent. nitrogen, with a zinc content of 86.83 per cent. Although the temperatures employed were ordinarily 200° above the melting-point of zinc, zinc placed in a combustion tube heated to this temperature in a current of ammonia did not melt but retained the form of the material as it was placed in the tube. It became brown and dust-like on the surface and as the percentage of nitrogen increased became blacker. The nitride obtained from the zinc dust and which contained 10.6 per cent. of nitrogen was a powder, mostly black but mixed with a brown material. It was found possible to remove considerable of the brown powder by washing in alcohol, the brown powder staying in suspension and being poured off with the alcohol. The black powder remaining was washed with ether and dried *in vacuo* but it was noticed that the odor of ammonia was very

[1] This Journal, 27, 373.

noticeable when the desiccator was opened, and the percentage of nitrogen had not been increased by the washing process.

The decomposition of the ammonia in the synthesis of this nitride at 600° was only from 1.0 to 1.5 per cent. so that it did not seem that the hydrogen would have caused any very important reversal of the reaction. The stability of the nitride when heated in an atmosphere of nitrogen was tested at different temperatures. Samples heated to 650° and 700° for an hour did not change appreciably in appearance or in percentage of nitrogen. However, sublimed zinc in the cooler parts of the tube showed that there had been decomposition, but that it had proceeded no more rapidly than the sublimation of the zinc. The following series of experiments was then undertaken.

Duration of heating.	Temp.	Loss of weight of nitride. Per cent.
20 min.	800–840°	60.1
1 hr.	750	63.0
1 hr.	700	26.0
1 hr.	600	6.3

These experiments show that the decomposition of zinc nitride begins below 600°, which is the temperature at which it may best be formed by the action of ammonia upon the metal, and that therefore it will not be possible to synthesize in this way a nitride of theoretical composition. The closest approach to it will be made by offering the greatest extent of metallic surface to the action of the ammonia, and thus accelerating the reaction. The higher absorption of nitrogen when the zinc was in the form of dust agrees with this view. The instability of the nitride at relatively low temperatures also indicates that it is useless to hope to bring about any considerable formation of nitride by direct union of the elements, although from the close relationship of zinc and magnesium in the periodic system, it had been hoped that zinc like magnesium could be made to combine directly with nitrogen.

Arons[1] has noted a slight combination of zinc and nitrogen between the poles of an electric arc maintained between zinc electrodes in an atmosphere of nitrogen, and Rossel[2] has observed a similar phenomenon when zinc and calcium carbide are heated in the air, but the only record which we have found of the preparation of a

[1] Chem. Centr. 11, 643 (1899).

[2] Compt. rend. 121, 941.

nitride of definite composition is that of Frankland,[1] who by heating zinc amide to 200° obtained a nitride to which he gave the formula Zn_3N_2. This theoretically contains 12.52 per cent. nitrogen. The highest percentage obtained in our experiments was 10.6 per cent., but in view of the facts just noted concerning the difficulty of preparing a nitride of theoretical composition by the action of ammonia upon metallic zinc, it seems probable that the nitride obtained in our experiments should be regarded as Zn_3N_2+xZn. Whether this diluting zinc is to be regarded as a mechanical mixture or a solid solution is a point upon which we have no evidence except the fact that it was not possible by fractional solution to isolate either a definite nitride or to dissolve the nitride and leave a residue of zinc. Apparently, the nitride and its diluting zinc dissolved together which is, so far as it goes, an indication that the nitride is dissolved in the zinc as has been shown to be the case with nitride of chromium by Baur and Voerman.[2] The properties of our nitride of zinc agree with those given by Frankland.

The Action of Ammonia upon Aluminium.—The action of dry ammonia upon metallic aluminium was studied in the same way. The most favorable temperature for the absorption of nitrogen seemed to be higher than was the case with zinc and only relatively slight amounts of nitrogen were fixed. Only a trace of nitrogen was found in aluminium dust which had been heated for an hour and three-quarters at 600° in a stream of ammonia whose decomposition was only 0.4 per cent. At 750° in an hour and a quarter 1.54 per cent. of nitrogen was fixed, the decomposition of the ammonia being 1.0 per cent. The highest percentage of combined nitrogen was obtained at a temperature of 700°. After three hours the amount of nitrogen was 1.80 per cent. The nitride is decomposed by boiling water with evolution of ammonia. The fixation of nitrogen by aluminium was so small that it was not deemed practicable to determine its temperature of initial decomposition in an atmosphere of nitrogen.

Nitride of Iron and Action of Ammonia upon Iron.—The formation of nitride of iron through the action of ammonia upon metallic iron has received a great deal of attention in recent years. The very interesting experiments of Baur and Voerman before alluded

[1] Phil. Mag. [4] 15, 149.

[2] Z. physik. Chem. 52, 467.

to have shown that the dissociation pressure of the nitride at the lowest temperature at which ammonia will react with iron is many atmospheres, and that therefore it will never be possible in this way to attain a nitride of theoretical composition. It would be expected from analogy with the other bivalent elements, magnesium, barium, zinc and others, that the formula for the iron nitride would be Fe_3N_2. The usually accepted formula is Fe_2N, based entirely upon the analytical results, which show as the highest amount of combined nitrogen which has been obtained a trifle less than the 11.11 per cent. required for the compound Fe_2N. Our experiments have been no more successful than those of others in synthesizing a nitride with a higher percentage of nitrogen. The best results were obtained from iron reduced by hydrogen which, from its large surface, absorbed nitrogen rapidly.

This spongy iron begins to decompose ammonia below 400°, and at 412° in spite of a rapid stream of gas flowing through the apparatus, 1.0 per cent. of the ammonia was decomposed. That nitrogen was being absorbed was shown by the fact that the gas passing the acid of the nitrometer was 87.6 per cent. hydrogen instead of the 75 per cent. obtained when NH_3 is decomposed by heat alone. The next gas analysis made when the furnace temperature was 440°, showed that the ammonia was decomposed to the amount of 3.4 per cent. and that the nitrogen was being almost quantitatively absorbed, the gas collected containing 96.2 per cent. hydrogen. The next test was made at a temperature of 513° and showed that nitrogen was being given off more rapidly than it was being absorbed, the gas in the nitrometer containing only 70.2 per cent. hydrogen. The proportion of ammonia decomposed was 12.8 per cent. The furnace was then allowed to cool with the ammonia passing through it. The nitride obtained contained 8.26 per cent. nitrogen. The most successful temperature was found to be 450–475°, but our best preparation yielded only 10.1 per cent. nitrogen, which is a few tenths of a per cent. less than some others have obtained. Varying percentages below this could be obtained according to the conditions.

Each of the preparations was analyzed by solution in dilute acid with measurement, and in many cases analysis of the gas evolved, titration of the dissolved iron, and distillation of the ammonia. The gases were always found to be pure hydrogen

and the sum of the iron and nitrogen to be above 99 per cent. If the hydrogen evolved during solution be calculated to free iron, and the difference between this figure and 100 per cent. called nitride, and the total amount of nitrogen be figured as being contained in this nitride, it will bring the percentage of nitrogen in the nitride to 14.5 per cent. as the average of determinations on nine samples, with a maximum of 15.1 and a minimum of 14.2. The percentage of nitrogen calculated on the total weight varied in these samples from 2.25 to 10.04, so that as far as analytical results show there is no break in the series, whose members may be regarded as either a mechanical mixture or a solid solution of iron and nitride of iron. The nitride of iron mentioned above corresponds closely to Fe_3N_2 containing 14.35 per cent. nitrogen. The series might then probably be considered as Fe_3N_2+xFe, but so far as percentage calculations go, might equally well be considered Fe_2N+yFe.

An analogy suggests itself between the nitride of iron and the carbide of iron. It is impossible to prepare the theoretical Fe_3C by direct union of carbon and iron. The resulting compound invariably carries a lower percentage of carbon. The theoretical carbide may however be isolated from any sample of slowly cooled iron which contains carbon, and we know that all such samples of slowly cooled steels are mechanical mixtures of iron and carbide of iron. This has been shown for steel in several ways but unfortunately the methods which have proven themselves most valuable in the investigations of the reactions of carbon and iron are inapplicable in the study of the nitrides, whose spontaneous decomposition prevents the study of cooling curves, and whose physical state as brittle fine wires or powder prevents the polishing necessary for a microscopic investigation. The impossibility of getting a solid bar of iron containing a high percentage of nitrogen prevents the application of the electrolytic method by which iron is dissolved away, leaving a pure carbide. An experiment was tried with a piece of sheet iron containing about 4.0 per cent. of nitrogen but no nitride could be isolated by electrolytic solution.

Solutions of the double chlorides of copper and potassium both neutral and slightly acid have proved useful in isolating some of the constituents of steel and their effect was tried on the nitrides. A qualitative test with nitrides containing 1.0 and 2.5 per cent. of

nitrogen showed them to be quickly attacked by a neutral solution. A sample with 6.2 per cent. nitrogen was slowly attacked while one with 8.0 per cent. of nitrogen was apparently unchanged even after two weeks. A quantitative experiment with a sample containing 8.2 per cent. nitrogen made from iron reduced in hydrogen was carried out by placing 0.100 gram of the nitride in a beaker with 10 cc. of neutral 30 per cent. potassium copper chloride. No copper was deposited nor was other sign of reaction visible, and after standing for six days at room temperature the residue was removed and analyzed. It had lost only 3 mg. in weight and contained 7.9 per cent. nitrogen as compared with the original 8.2 per cent. A parallel experiment made with a solution to which hydrochloric acid had been added until it was a decinormal solution, showed more marked action. After six days the powder had lost about 37 mg. in weight and its percentage of nitrogen was 7.05. Similar experiments with other nitrides confirmed these results. Nitrides with higher percentages of nitrogen were very slowly attacked, those with smaller percentages more quickly, but the concentration of nitrogen in the undissolved residue was practically unchanged. It seems almost impossible that this fine porous nitride could contain free mechanically mixed iron which would not be dissolved by neutral or slightly acid potassium copper chloride, reagents which will disintegrate and remove completely the iron even from white cast iron. The results far rather point to the conclusion that the material is practically homogeneous and that the nitrogen is probably present as a solution of nitride of iron in iron.

SUMMARY.

By the action of dry ammonia gas upon zinc dust at the most favorable temperature of 600° a nitride of zinc is formed. This has a marked dissociation pressure even at its temperature of formation and hence must always have a lower percentage of nitrogen than theory requires. Preparations were obtained with varying nitrogen content, the highest being 10.6 per cent. The formula Zn_3N_2 requires 12.5 per cent. nitrogen. The properties of our nitride agree with those of the Zn_3N_2 which Frankland obtained by heating zinc amide and it is to be regarded as a mixture, or solid solution, having the general formula Zn_3N_2+xZn.

When ammonia gas acts upon aluminium powder small amounts

of nitrogen up to 1.8 per cent. may be made to combine with the metal. The most favorable temperature is 700°.

The most favorable temperature for the formation of nitride of iron is 450–475°. On account of the high dissociation pressure of the nitride at this temperature the nitride formed must always contain less than the theoretical percentage of nitrogen. Preparations with 10 per cent. of nitrogen were scarcely appreciably attacked by neutral potassium copper chloride and although slowly attacked by acid solutions did not change their percentage composition. They can not therefore be mechanical mixtures of free iron and nitride and are preferably to be regarded as solid solutions, as is the case with nitride of chromium and chromium. From analogy with other bivalent elements iron should form the nitride Fe_3N_2 and the preparations may be represented by the formula Fe_3N_2+xFe.

UNIVERSITY OF MICHIGAN,
ANN ARBOR, July, 1906.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 100.]

THE ELECTROLYTIC PRECIPITATION OF GOLD WITH THE USE OF A ROTATING ANODE.[1]

BY JAMES RENWICK WITHROW.

Received July 30, 1906.

THE electrolytes used in this investigation were solutions of auric chloride in the presence of (1) potassium cyanide and (2) sodium sulphide. The rate of precipitation of the metal was especially studied. The results show that pure potassium cyanide is evidently a better electrolyte than sodium sulphide for this particular purpose.

The apparatus used in the experiments was similar to that described by Ingham.[2] The first series of experiments with the cyanide electrolyte was made under conditions prescribed by Exner.[3] They were as follows:

[1] From the author's thesis for the Ph.D. degree.

[2] This Journal, 26, 1269.

[3] Ibid. 26, 1256.

No.	Gold taken. Gram.	KCN. Grams.	Dilution. cc.	Current. Amperes.	Volts.	Time. Minutes.	Gold found. Grams.
1....	0.1377	1.5	103	5	13 –10.5	10	0.1377
2....	0.1377	1.5	78	5	11 –10.5	10	0.1372
3....	0.1377	1.5	78	5	10.5– 8.5	10	0.1372
4....	0.1377	1.5	78	5	10.5–10	6	0.1378
5....	0.1377	1.5	78	5	10.5– 9	4	0.1370

The deposits were washed without interrupting the current. Usually a liter of water was required for the purpose. They were of a beautiful gold-yellow color, and consisted of microscopic, very adherent needles. It was not found necessary to let them stand in a desiccator before weighing, but after the ether had been volatilized by the heat of the hand, the dish was rubbed with a chamois skin and placed on the balance pan where it came to a constant weight in a few minutes.

The results confirm Exner's observations in every particular. Even less time than mentioned by him is sufficient for complete precipitation.

To ascertain the minimum time in which it was possible to make a complete precipitation, the following trials were conducted:

No.	Gold taken. Gram.	KCN. Grams.	Dilution. cc.	Current. Amperes.	Volts.	Time. Minutes.	Gold found. Gram.
1....	0.2754	2.5	80	5	8– 7	10	0.2747
2....	0.2754	2.5	80	5		5	0.2706
3....	0.2754	2.5	80	5	7.6– 6.7	6	0.2720
4....	0.2754	2.5	80	5	7.5– 6.7	8	0.2754
5....	0.2754	2.5	80	7	9.5– 9	7	0.2748
6....	0.2754	2.5	80	10	14.5–13	2	0.2667
7....	0.2754	2.5	80	10	17 –13	3	0.2724
8....	0.2754	5.0	85	10	17 –10	3	0.2319
9....	0.2754	2.5	80	10	16 –12	3	0.2704
10....	0.2754	2.5	80	12	15	2	0.2476
11....	0.2754	2.5	80	10	15	4	0.2750
12....	0.2754	2.5	80	12	19 –12	3	0.2621
13....	0.2754	2.0	55	12–10	21 –18	3	0.2742

An inspection of this table reveals the fact, as seen in Expts. 1 to 4, that eight minutes are necessary to precipitate all of the gold. On increasing the current to seven amperes the gold was completely deposited in seven minutes. In the eleventh trial fifteen amperes were used and only four minutes were consumed in the deposition. In the trials from the sixth to the eleventh foaming of the electrolyte led to loss.

To learn the result of a still greater concentration of the electrolyte, the following experiments were carried out:

No.	Gold taken. Gram.	KCN. Grams.	Dilution. cc.	Current. Amperes.	Volts.	Speed per minute.	Time. Minutes.	Gold found. Gram.
1	0.2621	1.5	150	0.27–0.2	3.9	none	130	0.2621
2	0.2621	2.5	80	8 –5	11 – 7.5	800	10	0 2621
3	0.2621	2.5	55	12	18 – 8.5	800	3	0.2588
4	0.2621	2.5	30	12	11 – 6.5	800	3	0.2611
5	0.2621	2.5	30	12	13	800	3	0.2618
6	0.2621	2.5	30	12	11.5– 6	800	3	0.2602
7	0.2621	2.5	30	12	11 – 9.5	800	3	0.2608
8	0.2621	2.5	55	12	18 –10	800	4	0.2620
9	0.2621	2.5	55	10	16 –11	800	4	0.2604
10	0.2621	5	60	12	17 –10	800	3.5	0.2585
11	0.2621	2.5	55	12	21	800	1	0.0959
12	0.2621	2.5	55	12	25	800	2	0.2406
13	0.2621	2.5	55	12	16.5–10.5	800	4	0.2619
14	0.2621	2.5	55	12	14 – 9	800	4	0.2614
15	0.2621	2.5	55	12	14 –12	...	4	0.2600
16	0.2621	2.5	55	12	11 –10	380	4	0.2494
17	0.2621	2.5	55	12	15 –10	600	4	0.2571
18	0.2621	2.5	55	12	19 –13	800	4	0.2615
19	0.2621	2.5	55	12	17 –12	800	1	0.1265
20	0.0621	2.5	55	12	18 –11	765	4	0.2612
21	0 2621	2.5	55	12	19 –12	900	4	0.2612
22	0.2621	2.5	55	13	21 –12	790	4	0.2606
23	0.2621	2.5	55	15	12.5–10	450	4	0.2546
24	0.2621	2.5	80	15	14 –13	450	4	0.2412
25	0.2621	2.5	75	15	16 –10	740	4	0.2610
26	0.2621	2.5	80	15	16 –10	850	4	0.2611

The conclusion drawn from this series was that a current of not more than ten amperes should be used, the other conditions remaining the same. Higher currents produced boiling of the electrolyte. There was also variation in the speed of the rotator, and these two factors militated against getting constant results in the minimum space of time. In the succeeding determinations, therefore, only the conditions found most satisfactory in the last series were employed:

No.	Gold taken. Gram.	KCN. Grams.	Dilution. cc.	Current. Amperes.	Volts.	Speed per minute.	Time. Minutes.	Gold found Gram.
1	0.2611	2.5	80	7.0	10	800	12	0.2611
2	0.2611	2.5	80	10.2–10	11.4–10	800	5	0.2612
3	0.2611	2.5	80	10	14.7–9.6	860	5	0.2598
4	0.2611	2.5	80	10	10 –8	620	5	0.2527
5	0.2611	2.5	80	10	14 –9.6	820	7	0.2614
6	0.2611	2.5	80	10.2–10	10.8– 9	...	7	0.2609
7	0.2611	2.5	80	10	14 –10	820	10	0.2612
8	0.2611	2.5	80	10	14 – 9	770	10	0.2616

No.	Gold taken. Gram.	KCN. Grams.	Dilution. cc.	Current. Amperes.	Volts.	Speed per minute.	Time. Minutes.	Gold found. Gram.
9	0.2611	2.5	80	10	13 –9.5	800	7	0.2615
10	0.2611	2.5	80	10 –10.5	13.5–10	830	7	0.2611
11	0.2611	2.5	80	10	15 –12	795	1	0.1054
12	0.2611	2.5	80	10	13.5–9.5	850	2	0.2049
13	0.2611	2.5	80	10	13.5–9.5	815	3	0.2420
14	0.2611	2.5	80	10	15.5–10	820	4	0.2582
15	0.2611	2.5	80	10	14.7–9.6	860	5	0.2598
16	0.2611	2.5	80	10	14 – 9	810	6	0.2613
17	0.2611	2.5	80	10	14 –10.1	776	7	0.2614
18	0.2611	2.5	80	10	14 –10	830	7	0.2613

Beginning with Expt. 5, the current of ten amperes was regularly employed with an accompanying speed in the rotator of 800 revolutions per minute. The electrolyte was not previously heated from without. The points in the curve marked "KCN No. 1" in the figure were obtained from the eleventh experiment. Upon substituting a more concentrated gold solution—one containing 0.5222 gram—the final series was obtained:

No.	Gold taken. Gram.	KCN. Grams.	Dilution. cc.	Current. Amperes.	Volts.	Speed per minute.	Time. minute.	Gold found. Gram.
1	0.5222	5	60	10	10 –8	800	10	0.5216
2	0.5222	5	60	10 –10.2	10 –7.3	800	12	0.5226
3	0.5222	2.5	55	10 –10.8	14.5–9.6	800	10	0.5222
4	0.5222	2.5	55	10 –10.3	14 –9.4	810	12	0.5234
5	0.5465	3.5	60	10 –10.5	8.3–7	790	12	0.5461
6	0.5465	5	60	10 –10.2	9.3–8.3	790	1	0.1891
7	0.5465	5	60	10.2–10.5	8.3–7	800	3	0.4341
8	0.5465	5	60	10 –10.3	9.6–7.1	825	5	0.5286
9	0.5465	5	60	10	8.6–6.7	780	7	0.5437
10	0.5465	5	60	10.3–10	8.3–6.3	790	11	0.5468
11	0.5465	5	60	10	7.8–6.8	790	12	0.5467

From the first and second determinations it was seen that the gold was completely precipitated in ten to twelve minutes. No. 3 was then tried to see if less potassium cyanide could be used as it might exert a retarding influence on the rate of precipitation. The result was satisfactory but there was quite a perceptible deposit on the anode, resembling yellow pollen. This was probably an oxide of gold. It dissolved instantly in concentrated hydrochloric acid.

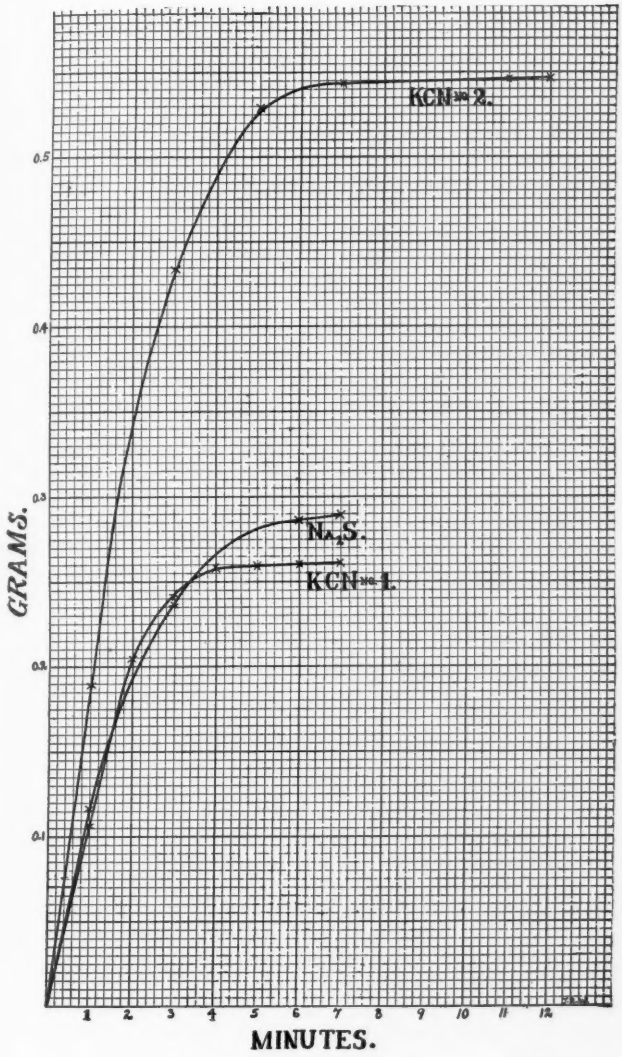
It may be mentioned here that this anodic stain or deposit was also noticed in several of the determinations, made with a station-

ary anode as checks on the work with the rotator. Especially was this so when the time of precipitation exceeded two hours. It was observed even with deposits weighing only 0.25 gram, with which amount it was never observed when the rotator was used, nor was it mentioned by Miller,[1] who, however, never precipitated more than 0.1697 gram of metal.

The anodic deposit having been eliminated by the use of an excess of potassium cyanide, the determinations from No. 6 on, furnished the points on the curve marked "KCN No. 2." Those deposits in which 0.5 gram of gold was completely precipitated were generally not so bright and were of a darker color than the 0.25 gram deposits.

Upon substituting sodium sulphide for potassium cyanide and electrolyzing the gold solution in its presence, very satisfactory results were obtained. The sodium sulphide was of the specific gravity 1.165. At the beginning, the gold solution was pipetted into a platinum dish and the sodium sulphide was added to it. This proved far from satisfactory because particles of gold sulphide adhered to the sides of the dish and it proved rather difficult to bring them completely into solution, so the expedient was adopted of first introducing the sodium sulphide solution into the dish, starting the rotator and then allowing the solution of gold chloride to run in from a pipette. No precipitate at all was formed and the liquid assumed a deep reddish brown or ferric sulphocyanide color, which, on heating, changed to a clear olive-green. The solution became cloudy during the decomposition from the separation of free sulphur. The anode was coated with a loose layer of sulphur. Rinsing with water sufficed to free the deposits from sulphur, after they were washed with hot water and dried in the usual way. The metallic deposits varied somewhat in color, that in Expt. 9 being beautifully burnished and rich yellow in hue. The curve marked Na_2S in the figure, was constructed from determinations made with 0.25 gram of metal in solution. It is worthy of note that the 0.25 gram curves in the two electrolytes—potassium cyanide and soldium sulphide—are almost identical. Probably they would have been exactly so if the same amounts had been used in each case.

[1] This Journal, 26, 1256.


KCN=2.
Na2S.
KCN=1.
GRAMS.
0.5
0.4
0.3
0.2
0.1
1
2
3
4
5
6
7
8
9
10
11
12
MINUTES.

No.	Gold taken. Gram.	Na_2S. cc.	Dilution. cc.	Current. Amperes.	Volts.	Speed per minute.	Time. Minutes.	Gold found. Gram.
1	0.2878	15	60	10 – 8.8	7.6– 7.2	810	7	0.2891
2	0.2878	30	60	10.1–10.3	6.9– 6	840	7	0.2879
3	0.2878	30	60	9.8–10.1	7.8	830	7	0.2897
4	0.2878	15	60	10 – 9.8	11.6–11.1	840	7	0.2898
5	0.2878	20	60	10	11.6– 9	800	7	0.2905
6	0.2878	30	60	10.2–10.5	8.8– 7.4	830	7	0.2883
7	0.2878	20	60	10.1–10	9.1– 8.2	850	7	0.2885
8	0.2878	15	60	10	11.5–10	840	7	0.2887
9	0.2878	30	60	10.1–10	9.4–8.5	850	1	0.1165
10	0.2878	30	60	10	8 –7	850	6	0.2870
11	0.2878	30	60	10 –10.2	9 –7.9	850	3	0.2365

It was also found that as much as 0.5 gram of metal could be completely precipitated in adherent form in a period of time not exceeding twelve minutes.

Another subject that received some attention was the electrolytic analysis of alkali halides. The complete determination of the components of such salts was shown by Smith to be quite possible when[1] using a mercury cathode and a silver-plated gauze as anode.

In an attempt to get iodine into an adherent deposit a rotator was used, thinking that the deposit might in this way be so compacted as to adhere firmly. The spiral cathode was accordingly rotated from 300 to 500 revolutions per minute, while a silver-plated dish was made the anode. The total dilution was about 70 cc. The following results were obtained:

No.	KI taken. Gram.	Current. Ampere.	Volts.	Time. Minutes.	Potassium found. Gram.	Potassium present. Gram.	Iodine found. Gram.	Iodine present. Gram.
1	0.0400	....	2.5–2.4	15	0.0094	0.0094	0.0280	0.0306
2	0.0400	....	2.8–2.7	16	0.0094	0.0094	0.0307	0.0306
3	0.0400	....	3.0–2.8	18	0.0095	0.0094	0.0300	0.0306

The cover glasses and the inner sides of the dish were washed down with distilled water shortly before the end of the determination. When the deposition was complete the dish was washed either by the usual siphoning method without interrupting the current or it was immediately withdrawn and the contents poured into a beaker and then rinsed several times with small portions of distilled water and dried in an air-bath, as was done with the gauze in the previous work. The former method was the safer

[1] This Journal, 52, 890.

of the two and was the one generally employed. In either case the wash-waters were carefully preserved and titrated for the potassium hydroxide.

Potassium chloride was tried in the same manner and very excellent, adherent deposits were quickly obtained.

No.	KCl taken. Gram.	Current. Ampere.	Volts.	Time. Minutes.	Potassium found. Gram.	Potassium present. Gram.	Chlorine found. Gram.	Chlorine present. Gram.
1.	0.0400	0.055–0.07	3.9–3.8	15	0.0207	0.0209	0.0190	0.0191
2.	0.0400	0.08	5	15	0.0208	0.0209	0.0206	0.0191
3.	0.0400	0.08 –0.08	3.8–3.4	10	0.0205	0.0209	0.0187	0.0191
4.	0.0400	0.08 –0.09	3.6	10	0.0205	0.0209	0.0192	0.0191
5.	0.0400	0.08 –0.09	4.2–3.8	10	0.0211	0.0209	0.0189	0.0191
6.	0.0400	0.08 –0.09	5 –4.7	10	0.0198	0.0209	0.0180	0.0191
7.	0.0400	0.08 –0.09	6.3–4.7	10	0.0211	0.0209	0.0187	0.0191

The same conditions were used as in the analysis of potassium iodide with aid of the rotator.

UNIVERSITY OF PENNSYLVANIA.

THE DISSOCIATION OF WATER VAPOR AND CARBON DIOXIDE AT HIGH TEMPERATURES.

BY IRVING LANGMUIR.

THE dissociation of gases at high temperatures has been the subject of many investigations during the past few years. In particular the states of equilibrium in the following reactions have been studied:

$$2HI \rightleftharpoons I_2+H_2.^{1}$$
$$CO_2+H_2 \rightleftharpoons CO+H_2O.^{2}$$
$$2SO_3 \rightleftharpoons 2SO_2+O_2.^{3}$$
$$2NO \rightleftharpoons N_2+O_2.^{4}$$
$$2CO_2 \rightleftharpoons 2CO+O_2.^{5}$$
$$2H_2O \rightleftharpoons 2H_2+O_2.^{5}$$
$$2NH_3 \rightleftharpoons N_2+3H_2.^{6}$$

[1] Bodenstein: Z. physik. Chem. **29**, 295 (1899).

[2] Hahn: Ibid. **44**, 513 (1903); **48**, 735 (1904).

[3] Knietsch: Ber. **34**, 4069 (1901); Bodenstein: Z. Electrochem. **11**, 373 (1905).

[4] Nernst: Göttinger Nachr. 1904, Heft 4.

[5] Nernst and v. Wartenberg: Göttinger Nachr. 1905, Heft 1; Löwenstein: Z. physik. Chem. **54**, 715.

[6] Haber and van Oordt: Z. anorg. Chem. **44**, 341 (1905).

There are two general methods of determining the dissociation constants of gases at high temperatures. First, by the measurement, at the desired temperature, of some property of the gas which varies with the dissociation and which can be measured without disturbing the equilibrium. Such a property is the density. The second method is to heat the gas to the desired temperature and then by rapid cooling or by the removal of some catalytic agent to decrease the velocity of the reaction to a negligible quantity so suddenly that there is no time for a perceptible change to occur in the composition of the gas during the operation.

Each of the above-mentioned investigations except that of Löwenstein depended on the use of the second method. In all these experiments there is necessarily some change in the composition of the gases during the cooling. The important question, and one usually very difficult of solution, is whether this change is so small as to be negligible; the whole value of the results depends upon its being so.

It occurred to Prof. Nernst that around a glowing metallic wire, in a gas capable of dissociating, there would probably be only very slight recombination of the dissociation products, during the short time required for these to diffuse from the surface of the wires out into the comparatively cold layers only a short distance from the wire. Furthermore, if the wire had a sufficiently strong catalytic action there would be equilibrium at the surface of the wire and hence the cold gas some distance from the wire would have the same composition as it would have were the whole gas uniformly heated to the temperature of the wire.

At Prof. Nernst's instigation I undertook a series of experiments in the laboratory of Physical Chemistry of the University of Göttingen to investigate the dissociation of gases around glowing platinum wires in the hope of finding this prediction fulfilled and of so obtaining a new and convenient method for the determination of the dissociation constants of water vapor and carbon dioxide. Prof. Nernst suggested determining the temperatures by means of the change of electric resistance of the wire.

I wish here to express my appreciation of the interest taken in the work by Prof. Nernst and to thank him for many valuable suggestions.

Several investigators have carried out experiments to study the reactions in gases near and on the surface of glowing wires. For

example, recently, Haber and van Oordt[1] showed that traces of ammonia are produced when a mixture of hydrogen and nitrogen is passed over an iron wire heated to a bright red heat by an electric current. Emich[2] has shown that nitric oxide is slowly decomposed when brought in contact with white hot platinum wires. v. Hoffman[3] led steam with great velocity over white hot platinum wires and so obtained considerable quantities of hydrogen and oxygen.

All such experiments, however, have given only qualitative results. The reason that no quantitative determinations of the dissociation or association of gases by this method have been made is probably due partly to the difficulty of the determination of the temperature of the glowing wire and partly to the fact that no one foresaw that the degree of dissociation obtained by this method would really correspond to the equilibrium at the temperature of the wire.

Since I began these experiments Prof. Nernst, who has been endeavoring to get several independent ways of determining these very important constants, has published in conjunction with Dr. von Warterberg papers on the dissociation of water vapor and carbon dioxide. The experiments there described were carried out by passing the gases through porcelain tubes, shaped like pipettes, in an electric furnace. The difficulties to be overcome were so great that it seemed that the method of glowing wires would have many advantages.

Another method, also suggested by Nernst, was used in the investigation of Löwenstein who used "semipermeable membranes" of platinum to measure the partial pressure of hydrogen in water vapor heated in an electric furnace.

APPARATUS.

The apparatus used (see Fig. 1) for my experiments consisted of a difficultly fusible (Durax) glass tube of 0.9 cm. internal diameter, in the center of which a fine platinum wire was stretched. A little above the lower end was a bulb to give room for the electric connections. In order to measure the resistance of the wire accurately it was necessary to determine the ratio of "drop" to current between two points on the uniformly glowing wire.

[1] Loc. cit.

[2] Monatsh. 13, 78 (1893).

[3] Ber. 23, 2, 3314 (1890).

There were four platinum wires, A, B, C and D (0.3 mm. diameter) sealed into the glass. The wires A and B were used for supplying the current and C and D to measure the voltage between the two points P and P'. To avoid errors due to poor contacts one

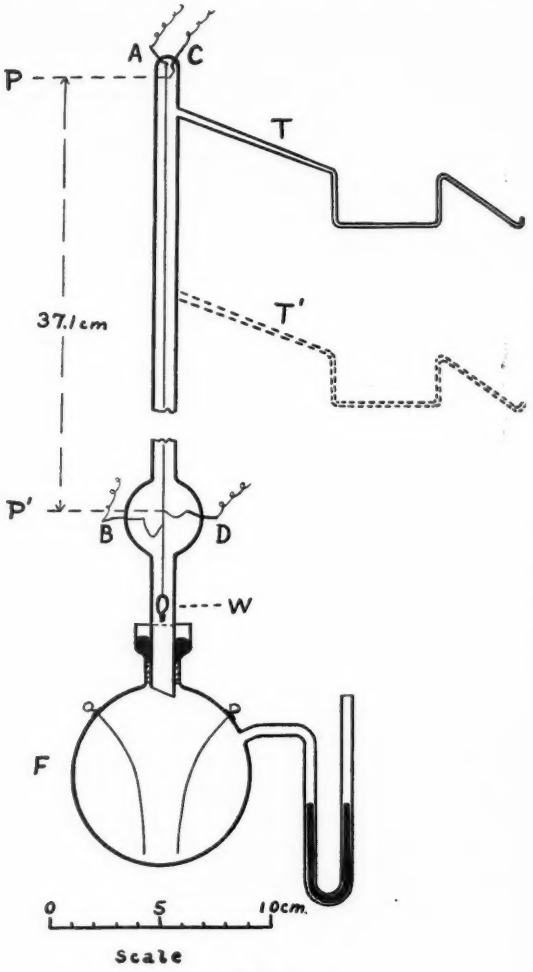


Fig. 1.

end of the main wire was fastened to C with silver solder and the other end similarly fastened to D. To A was soldered a short piece of wire, of the same kind as the main wire, and the other end of this was twisted around the main wire near its end so that the twisted part came between P and C. At P′ a short piece of wire was twisted with the main wire so the twisted part was between P′ and D. The other end of this piece had a small weight, W, of heavy platinum wire (about 2 grams) fastened to it to keep the main wire straight. A short distance below P′ a piece of wire was twisted around the wire P′W with the twisted part down and the end of this short piece was soldered to B. All the twisted parts were carefully welded. The wire in the path of the current was thus made of the same diameter everywhere from A to B and glowed uniformly when heated by the current. The portion PA was made shorter than PC so that the tension of the wire insured good contact at P.

In the bulb the connections BP′ and DP′ were made sufficiently long to allow for the expansion (about 4 mm.) of the wire when heated. The connection BP′ was made rather long, 1.5 cm., so that the gas upon entering the bulb would be rapidly heated to the temperature prevailing in the tube above, notwithstanding the cooling effect of the relatively large surface of the bulb.

When the wire was made to glow by an electric current, the temperature, to judge by the intensity of the emitted light, seemed to be perfectly uniform from A to B except within a distance of about 0.5 mm. from P and P′. But even at these joints themselves the wire would show a bright red heat when the rest of the wire was white hot.

The main wire was of the purest platinum that could be obtained from Heraeus. It had a diameter of 0.06 mm.

At the upper end of the tube a side tube, T, was attached. The internal diameter of this tube varied from about 2 mm. where it joined the main tube to about 0.6 mm. in the bent part. The object of bending it into the shape shown in the figure was to allow it to dip under the surface of the water in a beaker so that the water vapor passing through the apparatus would be condensed and could be collected over mercury together with any oxygen and hydrogen produced. The condensation occurred only after the first bend, that is, where the tube dipped under the water. The high velocity of the gases and the length of the

straight part of the tube prevented any hydrogen and oxygen diffusing back into the main tube.

The side tube T was joined to the main tube about 3 cm. below the end of the latter to avoid a possible change in the composition of the gases, due to the recombination of the dissociation products on the cooler platinum surfaces at the top of the tube. To be certain that this length of 3 cm. was sufficient to avoid error, one apparatus was made in which there were two side tubes, T and T′, but it was found that the gases from each had the same composition.

In the experiments the apparatus was set up with the main tube vertical; the connections A and C were bent by means of a long glass rod so that the wire was exactly in the middle of the tube.

EXPERIMENTS WITH WATER VAPOR.

The steam was generated from a flask connected by a mercury seal directly below the main tube of the apparatus. In the flask were two electrodes of platinum wire to produce hydrogen and oxygen, if desired, along with the steam. In this way the equilibrium could be reached from both sides. The water in the flask contained a little sodium hydroxide to give it sufficient conductivity. The rate of boiling was regulated by a small flame, and the flask enclosed in an asbestos box. The heat given off by the wire prevented any condensation of the steam until it had passed under the water around the tube T. The water and the dissociation products were collected in a calibrated eudiometer which contained 3 cc. and which was subdivided to 0.02 cc.

The volume of gas and water was read off, then the gas exploded and a reading again taken. Then a little air was added and usually there was another explosion when sparks were passed. In this way the amount of hydrogen, oxygen and other gases could be determined. These results were corrected for temperature and pressure and solubility of the gases in water. As there was often a considerable excess of hydrogen it was necessary in some cases to consider the partial pressures of each gas in making the correction for solubility. As an example of this calculation let us take the data of one experiment (No. 67) and calculate the dissociation.

2.761 cc. water and 0.182 cc. gas were collected over mercury. The mercury and water column below the gas were equivalent to 2.8 cm. mercury. After the first explosion the gas volume was 0.096 over a column equivalent to 3.3 cm. mercury. Air was

now added until the volume was 0.420 (over 1.6 cm. mercury). Finally, after another explosion the volume was 0.318 (over 2.1 cm. mercury).

The barometer read 74.1 cm. and the temperature was 28°. The vapor-pressure of water at this temperature is 2.8 cm. mercury. The pressures of the dry gases for each of the four readings of volumes were 68.5, 68.0, 69.7 and 69.2 cm.

The volumes reduced to 0° and 76 cm. and the dry condition and calculated to the basis of 1 cc. of water are: Before first explosion, 0.054; after first explosion, 0.028; before second explosion, 0.125; after second explosion, 0.095.

Thus the decrease of volume (V_1) on the first explosion was 0.026 and on the second (V_2) 0.030.

The absorption coefficients in water are for O_2, 0.031;[1] for H_2, 0.018.

The pressure in the eudiometer was on the average 70 cm.; the volume of dissolved gases (at 0° 0.76 cm.) per cubic centimeter of water is then for H_2

$$\frac{70}{76}\,\frac{\frac{2}{3}(V_1+V_2)}{V_0}\times 0.018 = 0.011\,\frac{V_1+V_2}{V_0};$$

for O_2

$$\frac{70}{76}\,\frac{\frac{1}{3}V_1}{V_0}\times 0.031 = 0.0095\,\frac{V_1}{V_0}.$$

V^0 is the volume before the first explosion. In our example the dissolved gases amounted to 0.011 cc. of H_2 and 0.0046 cc. of O_2 per cubic centimeter of water.

Altogether then there was $\frac{2}{3}(V_1+V_2)+0.011$ cc. hydrogen and $\frac{1}{3}V_1+0.0046$ cc. oxygen or 0.040 cubic centimeter of oxygen and hydrogen in the proportion to form water and an excess of 0.022 cc. of hydrogen.

The excess of hydrogen was rarely as large as in the above example and was observed only in the first few experiments after filling the flask F with water, or in the experiments in which the water was electrolyzed. The excess of hydrogen is due to the presence of traces of ammonia in the water or to the separation of peroxide of lead at the anode by the electrolysis of lead salts formed by the action of the sodium hydroxide on the glass.

The volume of other gases (nitrogen from the air or from the decomposition of ammonia) is found to be

[1] Landolt-Börnstein's tables.

$$V_o - V_1 - \tfrac{2}{3}V_2;$$

in our example 0.008 cc. per cubic centimeter of water.

The excess of hydrogen drives back the dissociation of the water vapor. We want in each case to know what the dissociation would be for equivalent amounts of hydrogen and oxygen. According to the law of mass action:

$$K = [H_2]^2[O_2];$$

since the concentration of the steam may be considered constant, now $[H_2]$ is proportional to $\frac{2}{3}G + E$ where G is the amount of gas of equivalent proportions and E is the excess of hydrogen. Similarly, $[O_2]$ is proportional to $\frac{1}{3}G$. If K′ is a new constant, we have

$$K' = G(G + \tfrac{3}{2}E)^2 = G_o^3$$

where G_o is the amount of oxygen and hydrogen which would be found if there were no excess of hydrogen. Solving for G_o and expanding in a series we get

$$G_o = G + E(1 - \tfrac{1}{4}E/G + \ldots\ldots).$$

In most cases it is sufficiently accurate to write

$$G_o = G + E.$$

If x is the degree of dissociation when there is no excess of hydrogen then, $x = \frac{2}{3}\,\frac{G_o}{1246} = 0.000535 \times G_o$. 1246 is the volume in cubic centimeters which 1 gram of steam would occupy at 0° and 76 cm. if the gas laws held down to 0°.

Returning to our example we have

$$G = 0.040 \qquad E = 0.022$$

$$\frac{1}{4}\,\frac{E^2}{G} = 0.003 \qquad G_o = 0.059$$

and $100\,x = 0.0032$.

EXPERIMENTS WITH CARBON DIOXIDE.

In the experiments with carbon dioxide this gas was prepared from marble and 50 per cent. chemically pure nitric acid in a Kipp's apparatus. The marble was boiled several times in weakly acidulated water to free it from air and the acid was freed from air by a stream of carbon dioxide. The gas was purified by passing through a saturated sodium bicarbonate solution then through concentrated sulphuric acid and finally through a long tube containing phosphorus pentoxide. This tube had a bulb at one end with two platinum wires sealed in it between which sparks from a powerful induction coil were passed. In this way

8 per cent. of carbon monoxide could be produced and in these experiments, too, the equilibrium could be reached from both sides.

The carbon dioxide apparatus was connected to the dissociation apparatus by means of a mercury seal.

The gases passing out through the tube T were collected in 33 per cent. potassium hydroxide solution contained in an apparatus described by Nernst.[1] The mixture of carbon monoxide and oxygen were measured in a eudiometer which formed the upper part of the apparatus; the amount of carbon dioxide was found from the increase in the weight of the whole apparatus. Then the gas was exploded and the contraction noted. The only corrections needed were for temperature and pressure.

No excess of carbon monoxide could be detected in any case. In order to avoid solubility of the gases in the caustic potash, this was first shaken with a mixture of carbon monoxide and air. The eudiometer was calibrated and contained 5 cc.

After the carbon dioxide apparatus was freed from air the gas was very pure; only one part in 10,000 to 20,000 by volume was not absorbed in the caustic potash.

The degree of dissociation was calculated from the formula

$$x = \tfrac{2}{3}\, G \times \frac{1.96}{1000} = 0.00131\, G.$$

G is the contraction on explosion (reduced to 0° and 76 cm.) per gram of carbon dioxide and 1.96 is the weight of a liter of this gas under standard conditions.

RESISTANCE OF THE WIRE.

In order to measure the temperature of the wire the resistance of the hot wire had to be measured and compared to the resistance at some lower temperature, 100° and room temperature being chosen. Thus the resistance had to be determined first with a current of 1 to 1.5 amperes flowing through it, and then with a current so small as to not perceptibly warm it. The Wheatstone bridge method could not well be used. The following method gave very satisfactory results and had the advantage that the resistance could be determined easily once every minute during the whole course of the experiment.

A constant resistance (N, Fig. 2) of 1.174 ohms was made of very thick constantan wire wound upon a large glass tube and the whole immersed in oil. A current of 1.5 amperes did not per-

[1] Nernst and v. Wartenberg: Göttingen Nach. 1905, Heft 1.

ceptibly warm this resistance. This known resistance and the wire in the dissociation apparatus were connected, by means of the wires A and B, in series, together with the variable resistance *r*.

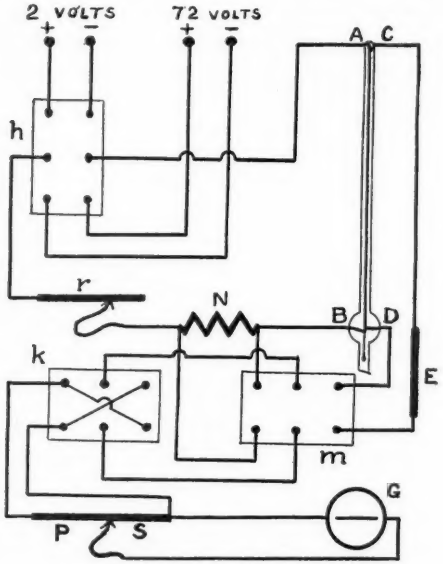


Fig. 2.

The two-way double switch *h* allowed either 2 or 72 volts to be used from a large storage battery, which gave a very constant current. The potential differences between C and D and between the two ends of N were then compared by means of the deflections obtained with a Deprez-d'Arsonval galvanometer, G. The resistances E, P and S were so chosen that the deflections were nearly equal for both potential measurements. *k* in the figure is a commutator and *m* a two-way double switch.

For measurements of the resistance at the various temperatures the following values of P S and E (in ohms) were used.

	P.	S.	E.
At room temperature.....	2000	500	20,000
At 100°.....	2400	500	30,000
At a red to white heat.....	2000	2	90,000

The resistance of the wire in the apparatus varied from 11 to

55 ohms, according to the temperature. The resistance of the galvanometer was 1077 ohms.

All resistances were carefully calibrated and the resistance of all connections measured and taken into account wherever these were not negligible. Although the system of wiring is rather complicated and a calculation of the resistance seems at first troublesome, it may be easily calculated from the formula

$$R = K - K\frac{\Delta e}{e_N}.$$

Here K is a constant to be determined once for all from the formulas

$$K = N\frac{E+P+S'}{P+S'}$$

$$S' = \frac{S}{1+\frac{S}{G}}.$$

e_N is the deflection of the galvanometer when connected with N.

Δe is the difference between e_N and the deflection when connection is made with C and D.

The possible sources of error such as thermocurrents, elastic lag in the galvanometer, lack of proportionality between the deflection and the current in the galvanometer, imperfect insulation, etc., were considered and by commutation, reading the galvanometer at regular intervals, and by a careful arrangement of the wiring such errors were avoided or eliminated as far as possible.

With these precautions the resistances are probably always accurate to one part in 1,000 and usually to one part in 4,000.

The resistance at 100° was determined by boiling the water in the flask until all the air was driven out of the apparatus. The pressure of the steam was observed on the manometer on the side of the flask. A simple calculation shows that the conductivity of the water layer on the wire and on the walls of the tube can be entirely neglected.

STUDY OF THE ACCURACY OF THE METHOD.

Before proceeding with the determination of the temperature coefficient of the resistance, without which the temperature could not be accurately known, it seemed best to find out whether this

method for determining dissociations was capable of giving uniform and accurate results. For this purpose a series of about forty preliminary experiments were made.

Through an oversight of Heraeus a wire containing 10 per cent. rhodium was furnished in place of the pure platinum ordered, and only after the apparatus was constructed and several experiments had been made was it noticed that the temperature coefficient of the wire was much lower than that of platinum (only 44 per cent. as great). Since the temperature determination was not important for the preliminary experiments these were continued with the platinum-rhodium wire. The final series of experiments were made with platinum wire of exceptional purity as was proved by the high value of the temperature coefficient of the electric resistance (0.003909). This is a higher value than any that could be found in the literature except a practically identical value given by Holborn.[1]

Before each experiment the resistance of the wire at room temperature and at 100° was determined and then the resistance of the glowing wire measured several times in the course of the experiment.

The ratio of the resistances of the hot and cold wire served as a sort of temperature scale whose absolute value was not known. For the sake of convenience, however, let us speak of the temperature of the wire not as it is given in this scale, but as it was afterward found to be in the absolute scale, by comparison of experiments made with the two kinds of wires.

The results of the preliminary experiments and also a few facts about the usefulness of the method which were found from the experiments with pure platinum can be summarized as follows:

(1) The observed degree of dissociation x was the same whether the water was electrolyzed or not or whether sparks were passed through the carbon dioxide or not. This was true even when the temperature was as low as 1050° absolute and the current of gas as rapid as 0.6 gram H_2O or 0.3 gram CO_2 per minute.

(2) Within wide limits x was independent of the velocity (S) of the gas (in grams per minute).

In a series of experiments with steam the current was maintained constant and S was gradually increased from 0.09 to 0.6. The temperature of the wire and also x remained, however, en-

[1] Drude's Ann. 6, 242 (1901).

tirely unchanged. When S was increased still more, the temperature decreased somewhat because of the cooling effect of the cold gas; x also decreased. For example while S grew from 0.6 to 1.10 the average temperature of the wire fell 20° and x decreased 42 per cent. The temperature difference of 20°, however, corresponds to a decrease of x of 24 per cent.; that is, the error in x was 18 per cent. With this strong current of steam, one could easily see that the wire directly opposite the opening to the tube T (Fig. 1) glowed less brightly than the rest. The whole decrease of x was probably due to the recombination of the hydrogen and oxygen on this short (3 mm.) length of cooler wire.

From these experiments it appears that the equilibrium around the wire is reached with extraordinary rapidity. A value of S = 1.10 corresponds to 33 cc. of steam at 125° per second or a linear velocity of 52 cm. per second. When one considers that the surface of the wire is only 0.7 sq. cm. it seems remarkable that 33 cc. can reach equilibrium in one second.

In another paper I will attempt to show theoretically that from this rapid rate of formation and by application of certain formulas which I have developed,[1] the observed value of x cannot differ from the value corresponding to the true equilibrium by more than 10^{-12}; that is, the observed dissociation must be identical with the equilibrium value.

(3) The resistance of the wire decreases about 2 per cent., while the temperature coefficient between 20° and 100° increases somewhat upon heating the wire for the first time. Upon further heating the wire changes very little if heated only in steam. In all the experiments the platinum-rhodium wire was heated altogether about twenty hours at temperatures between 1200 and 1600° (abs.). During the first five hours the resistance increased about 1 per cent., but in the remaining fifteen hours remained constant within the experimental error.

In the experiments with pure platinum wire the resistance increased slowly but steadily (about 1 per cent. in a long series of experiments). The wire had, however, become somewhat elongated. If one assumes the density of the platinum remained unchanged then the following relation should hold between the change of resistance ΔR and the change of length ΔL.

$$\frac{\Delta R}{R} = 2\frac{\Delta L}{L}.$$

[1] Dissertation Göttingen, 1906.

During eleven experiments a wire of 37.1 cm. length stretched 1.1 mm. The calculated increase of resistance is 0.60 per cent. Actually, the resistance at 20° increased 0.59 per cent. and at 100° 0.70 per cent.; that is, nearly within the experimental error.

Naturally, such lengthening of the wire introduces no error if the temperature coefficient remains unchanged.

In the preliminary experiments it was found that the value of x that was obtained depended solely upon the value of the ratio of the resistances of the hot and cold wire. The length of time the wire had been in use made no difference in this result.

Thus, eight preliminary experiments made at a temperature of 1440° (abs.) and distributed among all the preliminary experiments showed only irregular differences with a probable error of 2.9 per cent. in x for a single observation which corresponds to a temperature error of 3.0°.

The pure platinum wire, however, showed a tendency to give slightly increasing values for x as it was used even though the ratio of the resistances was kept constant. It seems then that the temperature coefficient of the resistance of platinum-rhodium remains constant but that of pure platinum decreases very slightly with continued heating.

(4) The lowest temperature at which the dissociation can be measured is about 1270° (abs.) as the gas formed then dissolves nearly completely in the water. Perhaps by determining the dissolved oxygen by chemical means it would be possible to work at much lower temperatures. The upper limit is set by the disintegration of the platinum, and it appears that a measurement of the dissociation is a very sensitive method of detecting disintegration ("Zerstäubung") of the platinum. When once the platinum-rhodium wire had been heated to 1650° (abs.) all further experiments gave too small values for x. For instance, after the wire was heated twenty-five minutes at 1670° (abs.) an experiment at 1460° (abs.) gave a value of x only 67 per cent. of what had previously been obtained at the same temperature. The explanation of this is that very finely divided platinum is deposited on the walls of the glass tube and that recombination of the gases occurs by catalysis. No deposit could be seen on the tube, but it was found that if the walls of the tube were rinsed out with aqua regia the original results could again be obtained.

With pure platinum wires no disintegration was observed either

in steam or in carbon dioxide up to temperatures of 1550° (abs.). Hulett and Berger[1] showed that in air disintegration occurs even at 1073° (abs.). It is therefore very important in these experiments never to heat the wire when air is in the apparatus. As was found later, heating in air also changes the temperature coefficient of the resistance.

By application of the law of mass action the effect of pressure on the degree of dissociation may be calculated. It was found that the variations of the barometric pressure from the normal had so small an effect on the dissociation that it could be safely neglected.

TEMPERATURE COEFFICIENT OF THE RESISTANCE.

According to Callendar[2] and Heycock and Neville[3] and particularly Harker,[4] one should be able to measure temperatures up to 1000° with great accuracy from the resistance if this is known for the three temperatures 0° and 100° and 440°. If R_t is the resistance at the temperature t then the following should hold

$$t - \theta = \delta \left\{ \left(\frac{t}{100} \right)^2 - \frac{t}{100} \right\}$$

where

$$\theta = \frac{R_t - R_0}{R_{100} - R_0} 100,$$

and δ is a constant depending only on the purity of the platinum.

Holborn and Wien[5] measured the resistance of platinum wires up to 1600°. Unfortunately, the platinum they used was not very pure, since the temperature coefficient was only 90 per cent. of that which one gets from the wire that Heraeus now furnishes. Holborn and Wien found that above 1000° the resistance was a linear function of the temperature.

The resistance of the wire used in our dissociation experiments was determined at 0°, at 100°, and at the temperature of boiling sulphur. However, different values of δ were obtained for different treatments of the wire. The wire was first heated to a red heat in air to anneal it. The followng table shows the results of the tests on three wires.

[1] This Journal, **26**, 1512 (1904).
[2] Phil. Mag. **5**, 48, 519 (1899).
[3] Jour. Chem. Soc. Trans. **67**, 160 (1895).
[4] Proc. Royal Soc. **73**, 217 (1904).
[5] Wied. Ann. **56**, 360 (1895).

Wire No.	First heated to	During the time. Minutes.	R_0.	R_{100}/R_0.	$R_{444.5}/R_0$.	R_{1710}/R_0.	δ.
1.....	1640° (abs.)	15	1.0028	1.3909	2.6335	....	1.74
2.....	1640° "	10	1.0202	1.3884	2.6338	6.20	1.57
3.....	1470° "	16	1.0029	1.3902	2.6350	....	1.66
3.....	1470° "	10	1.0022	1.3896	2.6387	....	1.56
3.....	1820° "	4	1.0226	1.3880	2.6404	6.27	1.41

The resistances are accurate to 2 or 3 units in the fourth decimal place. R_{1710} is the resistance measured at the moment at which the wire melted when heated by a strong current. Since the temperature of the wire was not uniform (as the piece used was only 4 cm. long) the resistance measured must be considered only as a lower limit to the true resistance at 1710°, the melting-point of platinum.

The table shows that glowing the wire in air decreases the temperature coefficient between 0° and 100°, but increases it between 100° and 440°.

A comparatively large change in δ corresponds to a small error in the temperature determination. Thus if δ changes from 1.50 to 1.55 the calculated temperature at 1000° changes but 4°.

According to the table, when δ is large R_{100}/R_0 is also large and it thus happens that at high temperatures it makes very little difference which pair of values of δ and R_{100}/R_0 are chosen for the calculation of the temperature from R_T.

The final values chosen for a wire which had been in use a long time were

$$R_{100}/R_0 = 1.3900.$$
$$\delta = 1.55.$$

This method of determining the temperature of the wire by extrapolating from 440° is rather unsatisfactory and it was therefore used only as a control on the other method adopted. The results, however, may have an interest in themselves.

The final arrangement was to measure the resistance of the wire directly while it was being heated in an electric furnace. In order to avoid the errors due to the action of the air on the wire and to have conditions as nearly like those in the experiments as possible, a current of steam was passed through the furnace during the time of heating. The furnace consisted of a very thin-walled porcelain tube wound with platinum wire.

The wire which had been used in apparatus No. 5 was used for these measurements. After the last experiment (No. 86) had

been made the apparatus was broken and the wire removed, care being taken not to bend or stretch it.

The resistance of one piece of this wire was determined at 0°, 100° and 440°. Another piece about 3 cm. long was wound around a small porcelain tube of 3 mm. diameter such as are used for thermo-elements. The turns were about 5 mm. apart. In this tube was brought the junction of a thermo-element near the middle of the coiled wire. To each end of the wire wound on the tube two platinum wires were welded; these, insulated in porcelain tubes, led out of the furnace. This bundle of porcelain tubes and wires was then placed in the electric furnace. The porcelain tube of the furnace was then connected with a brass tube for preheating the steam, a gas-tight joint being made by means of asbestos paper and water glass. After the furnace was heated to about 200° the superheated steam was passed in a gentle stream through the furnace. The resistance was then measured with the same apparatus that was used for all the other experiments. Two series of measurements were made. The thermo-couple was calibrated at the melting-point of antimony 630.6° and then, before and after each series of resistance determinations the reading of the thermo-couple was taken at the melting-point (1064°) of a short piece of pure gold wire placed about 3 mm. from the junction of the thermo-couple.

By moving the thermo-element back and forth in the tube it was found that the temperature over the whole length of the coiled wire was uniform.

The resistance at 0° (calculated from the resistance at room temperature and the temperature coefficient) was not just the same before and after the heating but it increased about 0.6 per cent. in each series. If this change is distributed over the observations at various temperatures the values for R_0 are obtained that appear in the following table which gives the results of the experiments with the electric furnace.

V.	R_0.	R_T.	R.	T (abs.). Degrees.
7.513	1.638	6.495	3.965	1130
9.390	1.639	7.321	4.467	1298
10.63	1.642	7.816	4.760	1406
7.377	1.645	6.438	3.914	1117
9.391	1.646	7.390	4.490	1298
11.48	1.650	8.204	4.972	1477
9.33	1.654	7.375	4.459	1293

V is the voltage of the thermo-couple multiplied by 1000. The cold junction was at 0°. For the melting-point of gold V was found to be 9.83.

R is equal to R_T/R_0.

By plotting R and T one finds that up to T = 1400 the points lie in a smooth curve which does not differ very much from that obtained from the Heycock and Neville formula by using the values $\delta = 1.55$ and $R_{100} = 1.390$. At T = 1300° the difference is about 20°.

If the curve be drawn through the points at T = 1406° and 1477° it appears that the curvature at about T = 1350° is greater than at lower temperatures, whereas from Holborn and Wien's paper it ought to be practically a straight line at this temperature. It seems probable that the cause of this is a slight conductivity at this high temperature of the porcelain on which the wire was wound and that therefore the results for R are slightly too low. The curve was drawn through the points at 1200° and carried to higher temperatures with approximately the same curvature that it has from 1100° to 1300°. The distance of the points at 1400° and 1477° from the curve then corresponds to 8° and 10° respectively. The curve was so nearly straight between 1300° and 1550° that it could be represented by the following formula without appreciable error.

$$T = 344.4\ R - 247.$$

FINAL EXPERIMENTS WITH STEAM AND CARBON DIOXIDE.

With apparatus No. 4 a series of experiments were made to get the ratio of the dissociations of steam and carbon dioxide at different temperatures. Since this ratio varies very little with the temperature, it was not necessary to get the temperature accurately for these experiments. With apparatus No. 5 the object was to determine as accurately as possible the relation between the temperature and the degree of dissociation of water vapor, hence the wire of apparatus No. 5 was used for the determination of the temperature coefficient. The water was not electrolyzed and sparks were not passed through the carbon dioxide in these experiments for the preliminary work had shown such a treatment to be without material influence.

The results of these experiments are given in the following table. R is the ratio of the resistance of the hot wire to that at 0°. T is the absolute temperature. It was assumed that the

temperature coefficient of the wire in apparatus No. 4 was the same as that in apparatus No. 5.

EXPERIMENTS WITH APPARATUS NO. 4.

Pure Platinum Wire.

Experiment. Number.	S. g. gas per min.	R.	T (abs.). Degrees.	100 r.	A.	Average. A.	Remarks.
30	0.14	5.00	1474	0.0140	3.746	3.7420	H_2O
31	0.30	5.00	1474	0.0132	3.720		
33	0.25	5.15	1526	0.0225	3.753		
35	0.13	5.02	1481	0.0281	5.05	5.05	CO_2
36	0.18	5.26	1565	0.0642	5.05		
37	0.43	5.00	1474	0.0135	3.730	3.728	H_2O
38	0.48	5.00	1474	0.0134	3.727		
49	0.64	4.935	1451	0.0136	3.826	3.823	H_2O
50	0.35	5.165	1531	0.0270	3.812		
51	0.45	4.94	1453	0.0139	3.829		
52	0.42	4.64	1351	0.0050	3.825		
53	0.12	4.77	1395	0.0140	5.168	5.181	CO_2
55	0.18	4.77	1395	0.0144	5.176		
57	0.22	4.91	1443	0.0250	5.179		
58	0.20	5.07	1498	0.0471	5.201		
60	0.50	4.95	1457	0.0144	3.828	3.817	H_2O
61	0.46	5.18	1537	0.0270	3.792		
62	0.47	4.96	1460	0.0150	3.831		

EXPERIMENTS WITH WATER-VAPOR WITH APPARATUS NO. 5.

Pure Platinum Wire.

Experiment No.	S. g. gas. per min.	R.	T (abs).	100 r.	A.	Average. A.
67	0.30	4.559	1324	0.0032	3.755	
68	0.27	4.670	1360	0.0045	3.733	
69	0.25	4.781	1399	0.0067	3.731	3.753
70	0.26	4.870	1429	0.0100	3.780	
71	0.28	4.991	1471	0.0143	3.767	
77	0.32	5.007	1476	0.0150	3.769	
78	0.43	5.232	1555	0.0292	3.762	
79	0.30	5.206	1545	0.0282	3.780	
80	0.33	5.000	1474	0.0149	3.761	
81	0.33	4.893	1437	0.0106	3.775	3.778
82	0.35	4.770	1395	0.0072	3.783	
83	0.32	4.651	1354	0.0051	3.818	
84	0.31	4.564	1325	0.0033	3.765	
85	0.61	4.744	1386	0.0067	3.789	

Under A is a number obtained as follows: Nernst and v.

Wartenberg[1] give for the dissociation of steam at atmospheric pressure:

$$\log_{10}\frac{2(100\,x)^3}{(2+x)(1-x)^2}=$$

$$[11.51]-\frac{25030}{T}+2.65\log_{10}\frac{T}{1000}-0.00055(T-1000)$$

and for carbon dioxide

$$\log_{10}\frac{2(100\,x)^3}{(2+x)(1-x)^2}=$$

$$[9.54]-\frac{29560}{T}+2.97\log_{10}\frac{T}{1000}-0.00074(T-1000).$$

The numerical coefficients except those in brackets are all determined thermodynamically and do not depend in any way on the results of the experiments on the dissociation. Hence, for my experiments the same coefficients should apply if only new values are substituted for the quantities in the brackets. But it is more convenient to first simplify the expression. By neglecting x compared to 1 and by division by 3 we obtain for steam

$$\log_{10}x=A_{H_2O}-\frac{8343}{T}+0.88\log_{10}\frac{T}{1000}-0.00018\,(T-1000)\quad(1)$$

for carbon dioxide

$$\log_{10}x=A_{CO_2}-\frac{9853}{T}+0.99\log_{10}\frac{T}{1000}-0.00025\,(T-1000)\quad(2)$$

A_{H_2O} and A_{CO_2} are then to be found from the experiments; the same values should be obtained no matter at what temperature the experiments were made. From Nernst's experiments the values are

$$A_{H_2O}=3.83.$$
$$A_{CO_2}=5.18.$$

A change in A of 0.01 corresponds to a change in x of 2.3 per cent. A small error ΔT in the temperature measurement makes a corresponding error in the value of A (ΔA) which for temperatures not too far from $T=1400°$ is given by

for steam

$$\Delta T=-109\left(\frac{T}{1000}\right)^2\Delta A,\qquad(3)$$

for carbon dioxide

$$\Delta T=-93\left(\frac{T}{1000}\right)^2\Delta A.\qquad(4)$$

[1] Göttingen Nachrichten.

DISCUSSION OF THE RESULTS.

The values of A in general seem to be independent of the temperature and the velocity of the gas current S. Experiments in which the temperature is below 1400° (abs.) often give values of A which differ considerably from the mean, but these differences are so irregular that they are probably due simply to the relatively inaccurate determination of the very small quantities of gas appearing at these low temperatures.

The longer the wire has been in use, the larger the values of A become. As was mentioned before this change does not occur to an appreciable extent with platinum-rhodium wire. During the determination of the temperature coefficient the same change was undoubtedly going on. The value of A which corresponds to the temperature measurements is then somewhat larger than in Expts. 77–85. As the most probable value we may take

$$A_{H_2O} = 3.79.$$

From Expts. 30–38 we get

$$A_{H_2O} = 3.734 \qquad A_{CO_2} = 5.050,$$

and from Expts. 49–62

$$A_{H_2O} = 3.820 \qquad A_{CO_2} = 5.181.$$

The deviation of A_{H_2O} from the value 3.79 can only be caused by errors in the temperature measurement (ΔT). This error must naturally be the same for the experiments with carbon dioxide as for those with steam. Thus in equation (3) and (4) the values of ΔT are equal and we have

$$\frac{\Delta A_{CO_2}}{\Delta A_{H_2O}} = \frac{109}{93}.$$

For Expts. 30–38

$$\Delta A_{H_2O} \text{ is } 0.056;$$

therefore

$$\Delta A_{CO_2} = 0.066;$$

hence

$$A_{CO_2} = 5.116.$$

Similarly, Expts. 49–62 give

$$A_{CO_2} = 5.147.$$

Expts. 47–64 were much more carefully made than Expts. 30–38, and since too low results can occur much more easily than too high results the most probable value seems

$$A_{CO_2} = 5.15.$$

From these results for A_{H_2O} and A_{CO_2} with the help of (1) and (2) we can calculate the dissociation at all temperatures at atmospheric pressure. At exceedingly high temperatures one must substitute

$$\frac{x}{\sqrt[3]{\left(1+\frac{x}{2}\right)\left(1-x\right)^2}} \text{ in place of } x.$$

The following table gives the dissociations as calculated for various temperatures.

T (abs.).	100 x for H_2O.	100 x for CO_2.
1000	0.000028	0.000020
1200	0.000745	0.00093
1300	0.00266	0.00407
1400	0.00787	0.0146
1500	0.0197	0.0436
1600	0.0446	0.110
1700	0.0920	0.260
1800	0.170	0.546
1900	0.302	1.04
2000	0.504	1.84
2200	1.21	5.00
2500	3.38	15.6
3000	11.1	48.5

These values for the dissociation are 9.5 per cent., in the case of steam, and 7 per cent., in the case of carbon dioxide, lower than those of Nernst. These differences however correspond to temperature differences of only 8° and 6° respectively.

The possible sources of error in this method lie almost entirely in the measurement of the temperature. It seems probable that the error in the temperature determination is not over 5° and almost certainly not over 10°.

SUMMARY AND CONCLUSIONS.

First. It is shown that when water vapor or carbon dioxide is passed through a tube containing a glowing platinum wire, amounts of dissociation products are obtained which correspond to the dissociation equilibrium at the temperature of the wire.

Second. The degree of dissociation of water vapor and carbon dioxide were determined by this method and results were obtained which for water vapor were 9.5 and for carbon dioxide 7 per cent. lower than those previously obtained by Nernst by another method.

Third. In determining the temperature of the wire the temperature-coefficient of the electric resistance of pure platinum up to 1200° was measured.

Fourth. It was found that platinum and platinum-rhodium wires do not disintegrate perceptibly in steam or in carbon dioxide up to 1300°. At 1400° platinum-rhodium begins to disintegrate in steam.

The method of determining the dissociation of water vapor and carbon dioxide by means of glowing wires has many advantages. The apparatus is simple and the experiments are quickly made.

The great rapidity of cooling of the gases insures accurate results for every reaction where the substance of the wire has a strong catalytic action.

The only serious difficulty lies in the determination of the temperature of the wire. A modification of the method by which instead of a wire a platinum tube or other surface of platinum is used might be very useful in some cases. The outer surface of the tube should be exposed to the dissociating gas. The temperature could then be determined either by a thermo-element inside the tube or by optical methods.

For the determination of the dissociation under high pressures the method would present great advantages. It would be a difficult task to make a tube which could withstand very high pressure at 1300° or 1400°, but to heat a wire to that temperature in a tube containing gas at a very high pressure is a comparatively easy matter. Such an arrangement would be well adapted for the study of the formation of ammonia from the elements since not only the velocity of the reaction, but also the amount of ammonia corresponding to the equilibrium would be much increased by high pressure. A few rough experiments have been made with ammonia and it seems the method would be capable of giving good results.

Another case in which this method may be of use is in determining the temperature of platinum wires or other platinum bodies. As v. Wartenberg has shown, temperatures may be accurately determined by means of the dissociation of steam. If the object is platinum, it need only be surrounded by steam and some of the steam withdrawn and analyzed in order to determine the temperature accurately.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 13].

EQUILIBRIUM IN THE DEACON PROCESS.

BY GILBERT NEWTON LEWIS.

Received August 17, 1906.

IN THE well-known process for making chlorine, invented by Deacon, a mixture of air and hydrochloric acid gas is led over a rough surface impregnated with cupric chloride, kept at a temperature of about 400°. The cupric chloride acts only as catalyzer and may be replaced by the chloride of iron, nickel or cerium. The reaction is simply,

$$4HCl + O_2 = 2H_2O + 2Cl_2.$$

This reaction never runs completely to an end, but approaches a state of equilibrium which, according to the conditions of temperature and concentration, fixes a definite limit to the yield of chlorine which it is possible to attain.

Reliable data concerning this equilibrium have not been obtained hitherto. A number of investigations have been made to determine the yield of chlorine in the Deacon process under actual working conditions, in which ordinarily the gases are sent past the catalyzer too rapidly for the establishment of equilibrium. The most extensive research of this kind is one by Lunge and Marmier.[1] It seems not unlikely that at the highest temperatures at which they worked equilibrium was frequently reached. We shall return later to a consideration of their results.

The present investigation of this equilibrium was undertaken partly on account of the technical significance of the process, but more especially because a knowledge of this equilibrium enables us to find at any temperature the difference between the free energy of formation of hydrochloric acid and that of water, two data of fundamental importance in chemistry. In particular, this study will permit a new calculation of the potential of the oxygen electrode, for which I have recently found a value differing by more than one-tenth of a volt from the one commonly accepted.[2]

EXPERIMENTAL METHOD.

The thermostat used in the following experiments was a modification of one that I have previously described.[3] It consisted

[1] Z. angew. Chem. 1897, p. 105.

[2] This Journal, 28, 158 (1906); Z. physik. Chem. 55, 465 (1906).

[3] P. Am. Acad. 40, 719 (1905); Z. physik. Chem. 52, 310 (1905).

in a fused mixture of sodium and potassium nitrates, in nearly equal proportions, contained in a vessel of enameled iron.[1] This vessel was surrounded by asbestos cloth upon which an electric heating coil of nickel steel wire was wound. The whole was packed in loose asbestos in order to avoid too great loss of heat. A current passed continuously through this outer coil, sufficient to heat the thermostat nearly to the desired temperature. The remainder of the heating was done by another electric heater[2] which was directly immersed in the bath and connected with the thermal regulator.

This regulator consisted of a hollow steel cylinder, holding about 300 cc., from which a steel tube of small bore led out of the thermostat to a height of nearly two meters; at the upper end it was joined to a glass capillary. The whole was filled with mercury, which on expanding made contact with a platinum wire in the glass capillary and thus operated a relay which broke the current in the inner heating coil. On account of the height of the mercury column, the thermostat could be used at temperatures far above the boiling-point of mercury.

The thermostat was well stirred and gave entire satisfaction. Without any readjustment it would run night and day for weeks without changing in temperature as much as a degree.

The temperatures were measured with a mercury thermometer. In order to eliminate the correction for the exposed stem, the thermometer was surrounded by a glass tube, about 4 cm. in diameter, in which the liquid of the bath could be drawn up nearly to the top of the mercury column. The liquid was thus raised and lowered several times until the thermometer gave a constant reading. Under the same conditions the thermometer was standardized by comparison with an accurately calibrated thermocouple which was kindly placed at my disposal by Mr. R. D. Mailey.

The apparatus in which the experiments were carried on is sketched in Fig. 1. Inside the thermostat (dotted lines) was situated the chamber E in which the reaction occurred. It was a

[1] The ware known as agateware is the only one which I have found satisfactory for this purpose.

[2] This heater was made by the Simplex Electric Co., of Cambridge, Mass., and proved very serviceable. It was simply a resistance wire, wound with asbestos, and enclosed in a spiral tube of copper.

glass cylinder of about 200 cc. capacity, half filled with the catalyzer and then drawn out at both ends and sealed to stout capillaries, which led out of the thermostat. One of these tubes, *D*, connected with the reservoir *B*, which contained the mixture of oxygen and hydrochloric acid. This reservoir was a 10-liter bottle joined by a siphon to a similar bottle, *A*. The gaseous mixture was kept over strong sulphuric acid.

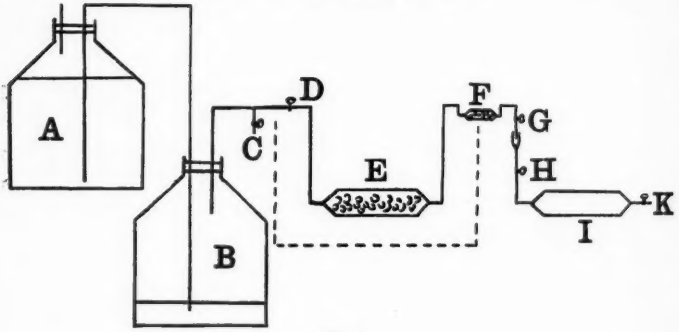


Fig. 1.

The hydrochloric acid was made from strong sulphuric acid and a solution of chemically pure hydrochloric acid. The oxygen was prepared by heating potassium permanganate. In the desired amounts these gases were introduced into *B* through *C*, forcing the sulphuric acid through the siphon into *A*, whence it later flowed back into *B* as the gas was drawn off. The hydrochloric acid dissolved somewhat in the strong sulphuric acid, and diffused through it, thus causing a slight change in the composition of the mixture from day to day.

The gas was introduced into the catalyzing chamber through *D* and after remaining there a suitable time was withdrawn for analysis through *F G*. As the gases were being removed the water vapor which was produced during the reaction showed a tendency to deposit on the colder part of the exit tube. Water thus condensed would dissolve considerable quantities of hydrochloric acid and thus vitiate the analysis. To avoid this difficulty, the tube *F*, containing glass beads saturated with strong sulphuric acid, was inserted in the exit tube. It was placed outside the thermostat, but near enough to be kept warm by it. The sulphuric acid soon became saturated with oxygen, chlorine and

hydrochloric acid, after which it allowed these gases to pass through in unchanged proportions, removing only the water vapor.

The bulb *HI* was so made that its end fitted over the end of the exit tube and could be made tight by a rubber connection. The gases from *E* were drawn into this bulb, after which it was removed and the gases analyzed, as will be described below.

The catalyzer was pumice stone, broken into pieces about the size of a pea, cleaned by boiling with hydrochloric acid, and then saturated with a 10 per cent. solution of cupric chloride. It was then dried in a current of dry hydrochloric acid gas at 250°, until it ceased to give off water. This frequently took several days. The last part of the drying was done inside the catalyzing chamber.

That part of the glass apparatus which came in contact with the fused nitrates of the bath proved very fragile and the work was much delayed by breakages. For very generous aid in the construction of several of the catalyzing cylinders I wish to express my thanks to Mr. C. A. Kraus.

The method of carrying out the experiments was as follows: The tube *I* was exhausted, stop-cocks *K* and *H* being open, *G* and *D* closed. *K* was then closed, and *G* opened for an instant, during which a certain amount of gas passed from *E* into *I*. After *G* was closed *D* was opened, allowing the gas from *B* to pass into *E*, where it was left for half an hour or more. The process was then repeated over and over in order to establish constant conditions in the catalyzing chamber and the drying tube *F*. When finally these constant conditions were reached the tube *I* was removed after each filling (stop-cocks *G H* and *K* being closed) and the contents analyzed for oxygen, chlorine and hydrochloric acid, in the manner described below.

Each time when the gas had been left in the catalyzing chamber for the desired time, and just before the tube *I* was attached for drawing off the gas, a manometer was joined to the end of the exit tube and the stop-cock *G* turned for an instant. This gave the pressure in E. A rough measurement sufficed, for a change in pressure affects the equilibrium but little.

The analysis of the mixture in *I* was made in the following way: The stop-cock *K* was opened under a solution of pure potassium iodide, about one-fifth normal, prepared from water freshly boiled and cooled. The bulb was then shaken until all the chlorine

and hydrochloric acid were dissolved. The gas remaining was nearly pure oxygen. It was measured in a gas burette, and then absorbed in pyrogallol in order to determine the amount of impurity.

The iodide solution was titrated with thiosulphate, about one-tenth normal, and when the iodine, which had been set free by the chlorine, was just neutralized, phenolphthalein was added and the same solution titrated with one-twentieth normal alkali (potassium hydroxide, with a little barium hydroxide). This method of successive titration with thiosulphate and alkali has been used by Lind.[1]

In this way the oxygen, chlorine and hydrochloric acid could all be separately determined. However, in all the later experiments, since it was found that the amount of oxygen present could be calculated with sufficient accuracy from the composition of the original mixture, only the ratio of chlorine to hydrochloric acid in the final mixture was determined. The procedure was then much simplified. It was no longer necessary to take pains to produce a thorough vacuum in the tube *I* before the gas was let in. Furthermore, it was no longer necessary to use a large volume of iodide solution and the titrations could therefore be made with greater precision.

The composition of the original mixture was determined as follows: The bulb *I* was attached to *C* and filled with gas from the reservoir at a pressure slightly above that of the atmosphere. One of the stop-cocks was then opened for a moment and the gas allowed to come to atmospheric pressure. Water was then allowed to run in until the hydrochloric acid was completely absorbed and the pressure was again that of the atmosphere.

During the whole process the bulb was kept at a known constant temperature. It was then weighed. From this weight, together with the weights of the bulb empty and full of water, the proportion of hydrochloric acid and oxygen could be readily determined, allowance being made for the pressure of aqueous vapor. In order to make sure that the gas left in the bulb was pure oxygen it was absorbed in pyrogallol. The volume of the residue never amounted to more than a small fraction of a per cent. of that of the original mixture and was corrected for.

[1] Dissert. Leipzig, 1905.

EXPERIMENTAL RESULTS.

For some time no concordant results could be obtained. This proved to be due to slow changes in the catalyzer. The method adopted does not permit the direct determination of the amount of water produced in the reaction. We assume that it is equivalent to the quantity of chlorine produced, but if the catalyzer gives up either water or chlorine this will not be true. It was found necessary, therefore, to pass a mixture of given composition over the catalyzer until the latter reached such a condition that it suffered no further change. At 352°, the lowest temperature at which experiments were made, several days were required, and frequently a week, before this stationary condition was reached

Just what the change in the catalyzer is I am unable to say, but the experiments showed that in the presence of a mixture containing a large excess of oxygen, considerable quantities of oxygen were taken up by the catalyzer. If later a mixture with an excess of hydrochloric acid was passed through, the oxygen was set free once more in the form of water. Probably in the first case the oxygen set free chlorine, forming an oxide or oxychloride of copper. In the second case this oxide or oxychloride united with the hydrochloric acid to form normal chloride again and water.

If the oxide (or oxychloride) and the chloride formed separate phases, there would be only one composition of the mixture of oxygen and hydrochloric acid which would permit the permanent co-existence of both phases. If, however, the oxide (or oxychloride) formed a solid solution, the catalyzer would have a different composition corresponding to every mixture of the gases.

We will make no assumption as to the composition of the catalyzer, nor as to its mode of action. We need only assume that when the measurements become concordant and remain so for some time the catalyzer has reached a condition of constant composition.

The first experiments at 352° were made with a mixture containing 92.7 mols. of oxygen to 100 mols. hydrochloric acid. After several days preliminary experiments showed that the catalyzer had reached constancy, ten consecutive measurements were made, the results of which are given in Table I. The extent to which the reaction runs may be expressed in various ways. Previous writers have denoted by x the fraction of the hydro-

chloric acid decomposed, or, in other words, the ratio of free chlorine to total chlorine in the final mixture. We will adopt this nomenclature. The values of x are given in the third column. The second column shows how long the gas was left in the catalyzing chamber.

TABLE I.

No.	Time in hours.	x.
1	1½	0.870
2	16	0.872
3	1½	0.871
4	1½	0.870
5	12	0.870
6	1½	0.868
7	1½	0.867
8	5	0.869
9	4	0.867
10	12	0.871
	Average,	0.8695

The preliminary experiments had shown that half an hour was not quite sufficient to establish equilibrium. It will be noticed that Expts. 1, 3, 4, 6 and 7 lasted one and one-half hours each, while the five others lasted from four to sixteen hours each. The average value of x for the first set is 0.8692, for the second, 0.8698. The close agreement of the two averages indicates that true equilibrium[1] had been reached in every case.

This experiment shows that at 352° this mixture containing 92.7 mols. of oxygen and 100 mols. of hydrochloric acid reacts until 86.95 per cent. of the hydrochloric acid is decomposed, when equilibrium is reached. In the final mixture there would therefore be 100 — 86.95 or 13.05 mols. of hydrochloric acid; $\frac{1}{2}\times$ 86.95 or 43.47 mols. of chlorine; also 43.47 mols. of water vapor; and 92.7 — $\frac{1}{4}\times$86.95 or 71.0 mols. of oxygen.

The average pressure in the experiments was very close to one atmosphere. The partial pressures of the four gases must be proportional to the above figures and their sum must equal unity. They are therefore, HCl, 0.0763; Cl_2, 0.2542; H_2O, 0.2542; O_2, 0.4152.

[1] In an experiment of this kind the fact that after a certain time a constant state is reached does not prove beyond question that equilibrium is reached. But this fact and the consistency of the results obtained at different temperatures and concentrations together show pretty conclusively that this is the case.

According to the mass law,

$$\frac{p_{Cl_2}^{\frac{1}{2}}\, p_{H_2O}^{\frac{1}{2}}}{p_{HCl}\, p_{O_2}^{\frac{1}{4}}} = K,$$

where K is a constant at any one temperature. Substituting the above values in this equation we obtain for K, the equilibrium constant at 352°, the value 4.15.

Another series of experiments at 352° was made in a new apparatus with fresh catalyzer. In this case the mixture contained 29.7 mols. of oxygen to 100 mols. hydrochloric acid. After the gas had passed through the apparatus for several days the measurements were begun. It was at once apparent that a longer time was required for the establishment of equilibrium than in the preceding case. Later experiments showed that in general the reaction progresses more slowly the greater the percentage of hydrochloric acid in the original mixture. This fact has also been inferred by Haber[1] from the experiments of Lunge and Marmier.[2]

With this mixture at least four hours was allowed for each experiment. Twenty-four experiments lasting, altogether, seven days gave concordant results. The last ten of these may be regarded as the best. They are recorded in Table II.

TABLE II.

No.	Time in hours.	x.
1	5	0.810
2	12	0.810
3	6	0.806
4	6	0.802
5	5	0.813
6	4	0.801
7	4	0.816
8	10	0.815
9	6	0.802
10	5	0.808
	Average,	0.808

The average pressure in these experiments was 0.93 atmosphere. Calculating as in the preceding case we find, $K = 3.95$.

The ratio of hydrochloric acid to oxygen in the final mixture was eleven times as great in this case as in the preceding. A small error in x is considerably magnified in K. Considering this fact and the slowness whith which equilibrium is attained at this temperature, the agreement between the two values of K at 352° may be regarded as satisfactory.

[1] Haber: Thermodynamik technischer Gasreaktionen.

[2] Loc. cit.

In better agreement were the two series at 386° recorded in Tables III and IV. Table V contains the results of a single series at 419°. At these temperatures, it will be noted, a shorter time was necessary for establishing equilibrium. In each series the catalyzer had reached a constant state for at least twenty-four hours before the experiments were begun.

TABLE III.

No.	Time in minutes.	x.
1	20	0.844
2	20	0.844
3	30	0.843
4	115	0.848
5	185	0.845
	Average,	0.845

Temperature 386°
Average pressure, 0.98 atmosphere.
Original composition, 327 mols. O_2 to 100 mols. HCl.

TABLE IV.

No.	Time in minutes.	x.
1	60	0.803
2	840	0.808
3	30	0.809
4	20	0.809
5	30	0.801
6	60	0.801
7	60	0.797
8	60	0.805
9	240	0.797
10	120	0.806
	Average,	0.804

Temperature 386°.
Average pressure, 0.96 atmosphere.
Original composition, 48.8 mols. O_2 to 100 mols. HCl.

TABLE V.

No.	Time in minutes.	x.
1	35	0.819
2	55	0.817
3	60	0.816
4	30	0.824
5	30	0.824
6	30	0.818
7	40	0.824
8	10	0.823
9	20	0.819
10	20	0.820
	Average,	0.820

Temperature 419°.
Average pressure 1.08 atmospheres.
Original composition, 327 mols. O_2 to 100 mols. HCl.

The results of all five series are collected in Table VI. The ratio of oxygen to hydrochloric acid in the final mixtures, given in the fifth column, is not used in the calculations but is given to show the range of the experiments.

TABLE VI.

No. of series.	Temp. Degrees.	Average pressure in atmospheres.	Mols. O_2 to 100 mols. HCl in original gas.	Mols. O_2 to 100 mols. HCl in final gas.	x.	K.
1	352	1.00	92.7	544.0	0.869	4.15
2	352	0.93	29.7	49.5	0.808	3.95
3	386	0.98	327.0	1970.0	0.845	2.94
4	386	0.96	48.8	146.0	0.804	3.01
5	419	1.08	327.0	1700.0	0.820	2.40

THERMODYNAMIC CONSIDERATION OF THE RESULTS.

It is evident from the preceding tables that the equilibrium constant, and, for a mixture of given composition, the yield of chlorine, are higher, the lower the temperature. This fact is in accordance both with the observations of previous experimenters and with the demands of thermodynamics, for the decomposition of hydrochloric acid by oxygen is accompanied by an evolution of heat. The amount of heat evolved in the reaction may be found from the heats of formation of hydrochloric acid and water.

The various determinations of the heat of formation of liquid water are reviewed in Ostwald's Lehrbuch. The three most reliable seem to be those of Schuller and Wartha,[1] of Than,[2] and of Thomsen.[3]

Schuller and Wartha burned hydrogen at atmospheric pressure in an ice calorimeter and obtained for the heat of formation of one mol. of water 68420 small calories.[4]

Than exploded oxygen and hydrogen in a bomb in the ice calorimeter. For 2 grams of hydrogen, 838.6 grams of ice melted. Taking 2.015 grams hydrogen as 1 mol. and using Smith's[5] value for the latent heat of fusion of ice, 79.9 cal., and adding the correction of 970 cal. calculated by Ostwald, we have 68480 cal.

Thomsen in a water calorimeter found 68360 cal. at 18°. This corresponds to 68500 cal. at 0°.

[1] Wied. Ann. **2**, 359 (1877).
[2] Ibid. **13**, 84 (1881).
[3] Pogg. Ann. **148**, 368 (1873).
[4] This value and all the following include the external work.
[5] Phys. Rev. **17**, 193 (1903).

The mean of these three determinations at 0° is 68470 cal. In order to find the heat of formation of water vapor the heat of vaporization must be subtracted from this quantity. The mean of the three values for the heat of vaporization of 1 mol. of water at 0° given in the tables of Landolt and Börnstein is 10750 cal. From the mean of five determinations of the heat of vaporization at 100°, and from the specific heats of water and water vapor we may calculate the latent heat at 0°. This gives the value 10680 cal. These two values are sufficiently concordant. Subtracting their mean from the heat of formation of liquid water at 0° and then dividing by two we find,

$$H + \tfrac{1}{2}O = \tfrac{1}{2}H_2O \text{ (vapor)} + 28900 \text{ cal.}$$

For the heat of formation of hydrochloric acid Thomsen[1] found,

$$H + Cl = HCl + 22000 \text{ cal.}$$

This value is also used by Berthelot, but whether or not he determined it independently I am unable to learn. This value is nearly independent of the temperature.

Subtracting the second of these equations from the first, we have

$$HCl + \tfrac{1}{2}O = \tfrac{1}{2}H_2O + Cl + 6900 \text{ cal.}$$

From the best determinations of the specific heats of these four gases it appears that the change in heat capacity during this reaction is zero, within the limits of accuracy of the experimental data. The heat of reaction is therefore independent of the temperature.

The change of the equilibrium constant with the temperature is given by the van't Hoff equation,

$$\frac{d \ln K}{dT} = \frac{-Q}{RT^2}, \qquad (1)$$

where K is the equilibrium constant in terms of partial pressures, T is the absolute temperature, R is the gas constant and Q is the total heat evolved when the reaction occurs at constant pressure. If Q is expressed in calories, $R = 1.985$.

When Q is independent of the temperature, as in the present case, equation (1) is, in its integrated form,

$$\ln K = \frac{Q}{RT} + C'$$

[1] Pogg. Ann. 148, 177 (1873).

where C' is the integration constant. Substituting the numerical values for Q and R and changing from natural to common logarithms, we have,

$$\log K = \frac{1509}{T} + C;$$

C is another constant which can be determined when K is known for any one temperature. It may therefore be found from each of the five results recorded in Table VI. The average of the five values of C thus obtained is -1.811. We have then finally,

$$\log K = \frac{1509}{T} - 1.811 \qquad (2)$$

This simple equation permits the calculation of the equilibrium constant of the Deacon reaction at any temperature. In order to show how well the experimental values of K contained in Table VI agree with theory, I have repeated them in Table VII by the side of the values calculated from equation (2).

TABLE VII.

Temperature. Degrees.	K (obs.)	K (calc.)
352	4.15	4.02
352	3.95	4.02
386	2.94	3.02
386	3.01	3.02
419	2.40	2.35

COMPARISON WITH OTHER DETERMINATIONS.

Haber,[1] in his excellent review of the work of Lunge and Marmier, concludes that true equilibrium was established in these experiments at the highest temperature at which they worked, 480°, and from their data he calculates, $K = 2.0$. Equation (2) gives 1.56 for this temperature. The discrepancy is doubtless due to the fact that in Lunge and Marmier's experiments at 480° the cupric chloride sublimed from the hot to the cooler part of the tube through which the gases were passing. Therefore the gases came in contact last with catalyzer considerably cooler than 480° and hence gave a larger yield of chlorine than corresponds to equilibrium at that temperature.

Another independent value of K at a very high temperature may be calculated from the experiments of Löwenstein[2] upon

[1] Loc. cit. p. 168.

[2] Z. physik. Chem. 54, 715 (1906).

the dissociation of water vapor and hydrochloric acid. Thus the dissociation constant of water is,

$$K' = \frac{p_{H_2}^{\frac{1}{2}} p_{O_2}^{\frac{1}{2}}}{p_{H_2O}^{\frac{1}{2}}}$$

and that of hydrochloric acid is,

$$K'' = \frac{p_{H_2}^{\frac{1}{2}} p_{Cl_2}^{\frac{1}{2}}}{p_{HCl}}.$$

Hence K, the equilibrium constant of the Deacon process, is equal to $\frac{K''}{K'}$.

Löwenstein finds at 1537° that hydrochloric acid is 0.274 per cent. dissociated into chlorine and hydrogen. From this we find, $K''=0.00137$. For water we find from Löwenstein's results, $K'=0.0074$ at 1510° and $K'=0.0122$ at 1590°. From these, interpolations by means of the van't Hoff equation give for 1537°, $K'=0.0103$. Dividing this by the above value of K'' we get, for the equilibrium constant of the Deacon process at 1537°, $K=0.133$.

From equation (2) we find $K=0.106$.

This is a very surprising agreement when we consider that the latter result was obtained by an extrapolation through more than 1100°.

THE ELECTROMOTIVE FORCE OF THE HYDROGEN-OXYGEN CELL.

From equation (2) we find for 25°, $K=1800$. We are now able to calculate the free energy of the Deacon process at 25°.

By a familiar theorem,

$$A = RT \ln K,$$

where A is the free energy (exclusive of this work done by the atmosphere) of the reaction,

$$HCl + \tfrac{1}{4}O_2 = \tfrac{1}{2}Cl_2 + \tfrac{1}{2}H_2O,$$

when the gases consumed and those produced are all at atmospheric pressure.

Substituting numerically for R, T and K, we find $A=4430$ cal. We may express this result in the form of an equation similar to those of thermochemistry.

HCl(1 atmos.) $+\frac{1}{4}O_2$ (1 atmos.) =
$\frac{1}{2}Cl_2$ (1 atmos.) $+\frac{1}{2}H_2O$ (1 atmos.) $+4430$ cal. (free energy).

The free energy of formation of hydrochloric acid may be calculated from the work of Dolazalek,[1] who measured the electromotive force between a hydrogen and a chlorine electrode immersed in a hydrochloric acid solution in which the vapor-pressure of hydrochloric acid was determined. The solutions ranged from five to twelve times normal. From Dolazalek's data Haber has calculated the free energy and found

$\frac{1}{2}H_2$(1 atmos.) + $\frac{1}{2}Cl_2$(1 atmos.) =

HCl(1 atmos.) + 22428 ± 118 cal. (free energy).

This value is for 30°, but the free energy and the heat of formation (22,000) are so nearly identical that the change of the former with 5° change of temperature is negligible. The same equation is true, therefore, at 25°.

Such free energy equations may be added and subtracted just like those of thermochemistry. Adding the two above equations, we have,

$\frac{1}{2}H_2$(1 atmos.) + $\frac{1}{2}O_2$(1 atmos.) =

$\frac{1}{2}H_2O$(vapor, 1 atmos.) + 26860 cal. (free energy).

From the free energy of a reaction it is easy to calculate the electromotive force of a cell in which this reaction occurs. In order to change from calories to volts we will use the same factor that Haber used in changing Dolazalek's data from volts to calories, namely 23110. Dividing 26860 by this number we obtain 1.162 volts as the electromotive force which a cell would have if its reaction consisted in the formation from oxygen and hydrogen at atmospheric pressure of water vapor at atmospheric pressure (assuming that it could exist at this pressure at 25°). Now the vapor-pressure of liquid water at 25° is 23.6 mm. of mercury. A cell converting hydrogen and oxygen into liquid water would have an electromotive force higher by $\frac{RT}{2} \ln \frac{760}{23.6}$, or, 0.045 volt. We therefore find for the electromotive force of the ordinary hydrogen-oxygen cell, 1.207 volts.

The accuracy of this value depends chiefly upon the accuracy of two data which we have used in the calculation. Error in the experimental determination of the equilibrium in the Deacon process could hardly lead to an error of more than a small fraction of a millivolt in this final result. On the other hand, an error of 200 calories in the value we have chosen for the heat of reaction in the

[1] Z. physik. Chem. 26, 334 (1898).

Deacon process seems quite possible and would produce an error of about 5 millivolts. It is possible too that Dolazalek's results may be far enough from the truth to give a similar error. On the whole, perhaps, we may regard the present determination as entitled to a little less weight than the value obtained in my previous paper,[1] namely, 1.217±0.010 volts.

The agreement between these two values, obtained in absolutely different ways, without a single datum in common, proves conclusively that the generally accepted value is about one-tenth of a volt too low.

At present we may take as the most probable value of the electromotive force of the hydrogen-oxygen cell, 1.212 volts, the average of the two determinations. I intend soon to review both these determinations with the aid of some new data and to compare them with the experiments of Nernst on the dissociation of water vapor and with those of Haber on the oxygen-hydrogen cell at high temperatures.

In conclusion I wish to express my deep obligation to Professor A. A. Noyes for generously placing at my disposal the means of carrying out this investigation in the Research Laboratory of Physical Chemistry, Massachusetts Institute of Technology.

SUMMARY.

Apparatus and method are described by which at the desired temperatures the conditions of equilibrium were obtained for the reaction, $4HCl + O_2 = 2H_2O + 2Cl_2$.

The catalyzer, cupric chloride, in each series of experiments required several days to reach a constant state, after which concordant results were obtained.

The time necessary to bring the gases to equilibrium was greater the lower the temperature and the smaller the percentage of oxygen present.

Experiments were made at three temperatures, 352°, 386° and 419°, and over a considerable range of concentration, the ratio of oxygen to hydrochloric acid in the final mixture being forty times as great in one case as in another.

At constant temperature the results are in accordance with the mass law.

The yield of chlorine from a given mixture is greater the lower the temperature, and the change of equilibrium constant with the

[1] This Journal, 28, 158 (1906); Z. physik. Chem. 55, 465.

temperature is in good agreement with the equation of van't Hoff.

A simple equation is given from which the equilibrium constant at any temperature may be calculated.

The value thus calculated for 1537° agrees with the results of Löwenstein on the dissociation of water and hydrochloric acid at that temperature.

From the equilibrium constant of the Deacon reaction at 25°, and the experiments of Dolazalek, the electromotive force of the hydrogen-oxygen cell at 25° is calculated to be 1.207 volts, while the value obtained by an entirely different method in a previous paper was 1.217±0.010 volts.

The conclusion of the previous paper, that the value at present accepted for the electromotive force is one-tenth of a volt too low, is thus fully corroborated.

LIQUID METHYLAMINE AS A SOLVENT, AND A STUDY OF ITS CHEMICAL REACTIVITY.

By H. D. Gibbs.

Received June 23, 1906.

Since Franklin[1] and his co-workers have shown, in an extended series of investigations, that liquid ammonia shows many analogies to water, both as a solvent and in its reactions, liquid methylamine would naturally be expected to show the same analogies to methyl alcohol. As $H.NH_2$ is to H.OH so is CH_3NH_2 to $CH_3.OH$. Owing to its intermediate position in the group $H.NH_2$, H.OH, $CH_3.NH_2$, $CH_3.OH$, one would expect methylamine to possess the property of existing in compounds as methylamine of crystallization to a degree corresponding to that of the other members of the group. The compounds in which water is known to be a constituent as water of crystallization are too numerous for mention; ammonia is a constituent of a large number of known compounds as ammonia of crystallization, and methyl alcohol possesses the property of uniting with many compounds as alcohol of crystallization. Among the latter which are mentioned in the literature are:

[1] Franklin and Kraus: Am. Ch. J. **20**, 820 and 836; **21**, 1 and 8; **23**, 277; **24**, 83; Franklin and Stafford: Ibid. **28**, 83; Franklin and Cady: This Journal, **26**, 499; Franklin and Kraus: Ibid. **27**, 191; Franklin: Ibid. **27**, 802.

$LiCl.3CH_3OH$;[1] $MgCl_2.6CH_3OH$;[1] $CaCl_2.4CH_3OH$;[2] $BaO.2CH_3OH$;[3] $3BaO.4CH_3OH$;[4] $SbCl_5.CH_3OH$;[5] $CuSO_4.CH_3OH$;[6] $5NaOH.6CH_3OH$;[7] $3KOH.5CH_3OH$;[8] $CH_3OH.H_2O$;[9] $CH_3ONa.CH_3OH$;[10] and various methyl alcohol addition products of $SnCl_4$, $FeCl_3$, $SbCl_5$, BF_3, SiF_4 described by Kuhlmann.[11] From these analogies it would be expected that many compounds, both organic and inorganic, containing methylamine of crystallization, can be prepared and experimentation has upheld this theory.

With these considerations in view, a study of the solubilities of a number of compounds in liquid methylamine, together with some of the reactions involved and qualitative measurements of the electrical conductivity of the solutions, has been undertaken. The results of quantitative conductivity measurements together with a description of the apparatus employed and a further study of some of the reactions which have not as yet been investigated will be described in later papers.

The liquid methylamine[12] employed in these investigations was the same as that used in the boiling-point determinations[13] and the same steel cylinder was used as a container. This steel cylinder is of about 500 cc. capacity and is fitted with an outlet tube and a tightly fitting needle valve. Methylamine, stored in sealed glass cylinders, is distilled into the steel cylinder, the connections being made by means of lead tubing of 0.5 cm. diameter attached to the glass with sealing-wax and to the steel cylinder by soldering to a steel screw connection made tight with lead washers. The glass tubes of about 100 cc. capacity containing the methylamine are cooled in a Dewar test-tube of liquid

[1] Simon: J. pr. Chem. [2] 20, 374.
[2] Kane: Ann. 19, 168.
[3] Dumas and Peligot: Ibid. 15, 10.
[4] Forcrand: Bull. soc. chim. 46, 337.
[5] Williams: Jsb. 1876, 332.
[6] Forcrand: Bull. soc. chim. 46, 61.
[7] Forcrand: Ann. chim. phys. [6] 11, 462.
[8] Göttig: Ber. 21, 1835.
[9] Forcrand: Ann. chim. phys. [6] 27, 547.
[10] Ibid. [6] 11, 455.
[11] Ann. 33, 208.
[12] Obtained from Kahlbaum through the kindness of the trustees of the Bache Fund, to whom acknowledgments are due.
[13] Gibbs: This Journal, 27, 851.

ammonia and one end is drawn down in the blast flame to about the size of the lead tubing so that when inserted into the lead tubing a snug fit is afforded. A minimum surface of the sealing-wax is thus exposed to the methylamine whose solvent action upon the wax is quite rapid. The steel cylinder is cooled in ice water, the valve opened and the glass tube of methylamine warmed in the air and finally in warm water, thus causing the methylamine to distil into the steel cylinder from which it can be conveniently redistilled into any form of apparatus and in any quantity desired.

The solubilities, qualitative measurements of the electrical conductivity of solutions of various substances in methylamine and the reactions which often take place were studied in closed tubes, the most convenient form of which is shown in Fig. 1.

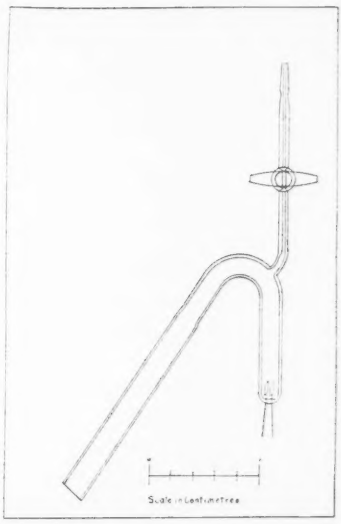


Fig. 1.

Platinum electrodes, sealed into one arm of the tube, are connected to the measuring apparatus by dipping the short platinum wires into mercury terminals. Solids are introduced into the other arm and sealed in. The tube, after exhaustion with the mercury pump is ready to be connected, by means of lead tubing and

sealing-wax, to the methylamine cylinder and the liquid distilled in. In order to permit of quantitative determinations, the tube is weighed after each of the operations described. Methylamine is first condensed in that arm of the tube which contains the electrodes (by cooling the arm in liquid ammonia) so that the electrical conductivity of the liquid can be measured. If any appreciable conductivity is shown, owing to the introduction of impurities, the determination is discontinued and the process repeated with a clean tube and fresh substance. The methylamine is brought in contact with the solid by slowly inverting the tube. If solution is effected, the conductivity is measured after pouring the solution back into the arm containing the electrodes. In the investigation of liquids and gases the tube is first sealed and exhausted and the liquid or gas introduced through the stop-cock. The Kohlrausch form of apparatus with bridge and telephone is employed for the measurements.

Crystallization of the compounds in solution is often effected by cooling the reaction tube in liquid ammonia. The excess of the solvent is in many cases easily and completely removed by spontaneous evaporation on opening the stop-cock. In other cases exhaustion with the mercury pump is necessary to remove traces which are mechanically held. Other substances break down under reduced pressure and give up methylamine which was held in chemical combination. This is especially noticeable in the case of certain aromatic hydroxyl compounds which not only unite with one molecule of methylamine for each hydroxyl group, but also crystallize with additional amounts of methylamine varying with the temperature and pressure. The temperature at which the substances under investigation and the methylamine are brought in contact is frequently an important factor in the character of the reaction. In the majority of the cases investigated the methylamine and other reacting substances were at the room temperature when brought in contact with each other. In many cases the rise of temperature caused by the reaction was sufficient to produce complicated and secondary changes which were not investigated. Quinone and the aldehydes, picric acid and other nitro derivatives are notable examples, and it is very probable that the reactions with these substances will be much simplified if carried on in the cold. Re-

sorcinol and quinol undergo complicated reactions with methylamine if contact occurs at the room temperature, while if the arm of the tube which contains the hydroxyl compound is cooled in liquid ammonia and the methylamine condensed therein, the reactions are quantitative and unaccompanied by the production of by-products.

The gain in weight of the reaction tube will in most cases, except when volatile products are formed as a result of the reaction, show the amount of methylamine which has entered into reaction. It is to be expected that this method of investigation will often give unsatisfactory quantitative results owing to impurities which may be present in the reacting substances and to the fact that in many cases the last traces of methylamine which are mechanically held are difficult of removal, and also it must be remembered that some of the reaction products break down slowly, constantly losing weight and giving up methylamine or other volatile products, and in other cases the reactions are evidently not quantitative. The amounts of methylamine of crystallization are in many cases difficult of determination by analytical methods for the crystals usually have low melting-points, effloresce at low temperatures and comparatively high pressures, and are difficult to obtain uncontaminated by the mother-liquors from which they are crystallized. No attempts to determine the composition of the crystalline compounds thus obtained, have been made by physicochemical methods. Therefore, the amount of methylamine of crystallization in combination, as determined from analytical data, can not in some cases be considered as definitely fixed.

The behavior of the substances under investigation was in each case studied as fully as circumstances at the time seemed to warrant. Some of the observed reactions have been carefully studied, the products recrystallized from other solvents and analyzed. In many instances, however, this has not been attempted, the reactions being manifestly complicated, leading too far afield, and perhaps better attempted as a separate piece of research.

EXPERIMENTAL PART.

The Hydrocarbons.—All of the hydrocarbons investigated are soluble in liquid methylamine, the solutions are colorless and

practically non-conductors of the electric current.[1] At the temperatures to which the solutions were subjected, namely from the room temperature to that of liquid ammonia (about 20° to about —33°), no evidence of a reaction was apparent.

Acetylene was found to be very soluble. Measured volumes of the gas were conducted into weighed quantities of methylamine. In one case 0.3584 gram of methylamine absorbed 18 cc. of acetylene. Normal pentane, toluene and metaxylene were found to be miscible in every proportion which was tried. Paraffin, triphenylmethane, diphenyl, naphthalene, anthracene and phenanthrene are all very soluble and crystallize readily from the solutions, no methylamine of crystallization being held in any case.

THE HYDROXYL COMPOUNDS.

Methyl alcohol is miscible in all proportions, the solution is colorless and conducts the electric current to some extent. As the alcohol is an electrolytic solvent it is possible that the conductivity is due to the dissociation of the methylamine. There is no evidence of reaction.

Isopropyl alcohol is miscible in all proportions, the solution is colorless and is practically a non-conductor of the electric current. There is no evidence of a reaction.

Tertiary butyl alcohol in the solid state dissolves very slowly. Upon raising the temperature above the melting-point of the alcohol (23.5°) the two liquids are found to be miscible in all proportions. The solid alcohol separates slowly when the concentrated solution is cooled. The solutions are colorless and practically non-conductors of the electric current. There is no evidence of a reaction.

Cetyl alcohol is very soluble, the solution is colorless and practically a non-conductor of the electric current. The alcohol can be crystallized from the solution. There is no evidence of a reaction.

[1] An arbitrary scale for expressing the results of the conductivity measurements was adopted.

Resistance less than 100 ohms.....very good conductor.
From 100 ohms to 200 ohms.....good conductor.
From 200 ohms to 500 ohms.....fair conductor.
From 500 ohms to 2000 ohms.....poor conductor.
From 2000 ohms to 5000 ohms.....very poor conductor.
Above 5000 ohms.....practically a non-conductor.

The solutions measured were usually quite concentrated and the cell employed was of about unit resistance capacity.

Glycerol is very soluble with marked rise of temperature. The solution is colorless and a fairly good conductor of the electric current. There is some evidence of a reaction taking place between the two liquids, although no reaction products were isolated. It is possible that the glycerol contained a little water but the assumption is not necessary to explain the conductivity, for both glycerol and methylamine are electrolytic solvents.

*Hydroxylamine hydrochloride** is very soluble but was not further investigated.

Phenol is very soluble with a slight rise of temperature. The colorless solution which is formed is a good conductor of the electric current. Upon cooling the solution, by means of liquid ammonia, there is slowly formed a fine crop of beautiful colorless crystals. These were purified by allowing the internal pressure to force the mother-liquor out through the stop-cock, after which they were melted, the solution cooled and the crystals allowed to again slowly form and the mother-liquor again removed. By repeating this operation a number of times a crop of crystals was obtained melting from 8.5° to 9.0°. The methylamine in these crystals was obtained by distillation with caustic potash, collecting the evolved gas in standard hydrochloric acid solution and titrating with standard ammonia solution, using methyl-orange as an indicator.

0.4054 gram substance gave 0.1480 gram methylamine.

$C_6H_5.ONH_3.CH_3.CH_3NH_2$, calculated CH_3NH_2 39.79, found 36.57.

*Orthonitrophenol** is very soluble, producing a yellow solution which was not further investigated. The ammonia compound $NH_4O.C_6H_4NO_2$ is described by Merz and Ris,[1] and its electrical conductivity in liquid ammonia solution has been investigated by Franklin and Kraus.[2]

Picric acid is very soluble with marked rise of temperature. The orange-red solution which is formed is a good conductor of the electric current. Upon expelling the excess of methylamine the solid, as it dries, changes from a deep red to a yellow-orange color. This compound is somewhat soluble in alcohol and very soluble in warm water. The aqueous solution deposits yellow

* All compounds marked with a star were investigated by Professor E. C. Franklin, and the results here recorded are taken from his unpublished notes.

[1] Ber. 19, 1752.

[2] Am. Ch. J. 23, 295.

crystals on cooling. These crystals were washed with alcohol and dried in a vacuum desiccator. They are not exploded by friction or shock. On heating they gradually turn red at 186° and at 195° decompose, turning black without melting. The reaction products are under further investigation. An addition product, $C_6H_2(NO_2)_3OH.NH_2CH_3$ has previously been prepared from aqueous, alcoholic or chloroformic solutions.[1]

Thymol is very soluble with a slight rise of temperature. The colorless solution which is formed is a fairly good conductor of the electric current. Upon removing the excess of methylamine with the mercury pump, a process which requires about six hours, some colorless crystals were formed upon cooling the thick viscous solution with liquid ammonia. The melting-point of these crystals is about 25°. Attempts to determine their composition gave no satisfactory results.

α-Naphthol is very soluble with rise of temperature. The colorless solution is a good conductor of the electric current. The uncombined methylamine is removed by spontaneous evaporation, leaving a thick liquid which solidifies to a mass of colorless crystals on cooling. Melting-point about 37°.

0.2360 gram of α-naphthol retains 0.1042 gram of methylamine. $C_{10}H_7.ONH_3CH_3.CH_3NH_2$, calculated CH_3NH_2 30.14 per cent., found 30.60.

This compound gives up a portion of its methylamine under diminished pressure, loses its crystalline form and becomes a white amorphous solid.

0.2360 gram of α-naphthol retains 0.0504 gram of methylamine. $C_{10}H_7.ONH_3CH_3$, calculated CH_3NH_2 17.74 per cent., found 17.60.

β-Naphthol is very soluble with rise of temperature. The solution which is formed is of a light yellow color, probably due to impurities, and is a good conductor of the electric current. The spontaneous evaporation of the uncombined methylamine leaves a viscous liquid in which no crystals could be induced to grow. At this point, 0.1682 gram of β-naphthol retains 0.0656 gram of methylamine.

$C_{10}H_7.ONH_3CH_3.CH_3NH_2$, calculated CH_3NH_2 30.14 per cent., found 28.05.

Upon diminishing the pressure this liquid gives up methylamine

[1] Delépine: Ann. chim. phys. [7], **8**, 461; Ristenpart: Ber. **29**, 2530.

readily until a second comparatively stable condition is reached. At this point still no crystals were obtained.

0.1682 gram β-naphthol retains 0.0337 gram of methylamine.

$C_{10}H_7.ONH_3CH_3$, calculated CH_3NH_2 17.74 per cent., found 16.7.

It is, of course, possible that the two conditions described do not represent definite compounds. It is probable, however, that crystallization may be effected by means other than those tried. Compounds with aniline, $C_6H_5NH_2.C_{10}H_7.OH$, and other allied substances have been produced.[1] Friedländer and Zakrzewski[2] have found that β-naphthylamine is produced on heating β-naphthol with ammonia.

Quinol is very soluble with a marked rise of temperature. The solution which is formed is a good conductor of the electric current. When methylamine and quinol react at room temperature the heat developed is sufficient to produce secondary reactions. When the quinol is cooled by immersing the reaction tube in liquid ammonia and the methylamine condensed upon the cold substance the reaction is not accompanied by the formation of secondary products. In the former case the solution is reddish brown, in the latter light pink. From the light pink solution on cooling there is obtained a beautiful crop of pink crystals. The color is probably not that of the pure compound.

0.6022 gram of quinol retains 1.4843 grams of methylamine.

$C_6H_4.(ONH_3CH_3)_2.6CH_3NH_2$, calculated CH_3NH_2 69.3 per cent., found 71.1.

These crystals melt considerably below the room temperature. When the methylamine is allowed to escape from this liquid another crop of pink crystals separates out.

0.6022 gram of quinol retains 0.3456 gram of methylamine.

$C_6H_4.(ONH_3CH_3)_2$, calculated CH_3NH_2 36.09 per cent., found 36.4.

These are comparatively stable at room temperature and atmospheric pressure but when the pressure is slightly reduced by suction of the water pump they slowly effloresce. The corresponding aniline addition product $C_6H_4(OH)_2.(C_6H_5.NH_2)_2$ has been prepared by Hebebrand.[3] With the mercury pump these crystals break down into a white solid.

[1] Dyson: J. Chem. Soc. 43, 469.

[2] Ber. 27, 763.

[3] Ibid. 15, 1973.

0.6022 gram of quinol retains at good vacuum 0.1672 gram methylamine.

$C_6H_4.OH.ONH_3CH_3$, calculated CH_3NH_2 22.02 per cent., found 21.7.

This compound without further purification melts at 105°, assuming a brilliant red color in melting; on cooling, it solidifies into a brilliant red crystalline mass. The compound is very soluble in water, the solution being a good conductor of the electric current. An aqueous solution of quinol is a very poor conductor. The compound is almost insoluble in ether while quinol is soluble. Methylamine is given off upon boiling the aqueous solution with potassium hydroxide solution.

Resorcinol behaves in a manner analogous to quinol. It is very soluble with rise of temperature, the solution is a good conductor of the electric current, and the reacting substances must be strongly cooled in order to prevent the formation of secondary products. The solution is light green in color and separates light green crystals on cooling.

0.6755 gram of resorcinol crystallized with 0.8945 gram of methylamine.

$C_6H_4.(ONH_3CH_3)_2.3CH_3NH_2$, calculated CH_3NH_2 58.5 per cent., found 57.

From other experimental data it seems probable that a compound with a larger amount of methylamine of crystallization is capable of existence. As the methylamine is allowed to escape from the melted crystals, another crop of beautiful light green crystals is formed. These are quite stable at atmospheric pressure and room temperature but not as stable as the corresponding quinol compound.

0.6755 gram of resorcinol retains 0.3542 gram of methylamine.

$C_6H_4(ONH_3CH_3)_2$, calculated CH_3NH_2 36.09 per cent., found 34.3.

These crystals give up more methylamine with the mercury pump, producing a white amorphous solid.

0.6755 gram of resorcinol retains at good vacuum 0.1807 gram of methylamine.

$C_6H_4OH.ONH_3CH_3$, calculated CH_3NH_2 22.02 per cent., found 21.1.

This compound without further purification melts at 95° to a red liquid which solidifies to brilliant red crystals on cooling.

Methylamine is given off on boiling with caustic potash solution. The corresponding ammonia compound $C_6H_4.OH.ONH_4$, has been previously prepared by passing dry ammonia gas into a solution of resorcinol in dry ether.[1]

Pyrogallol is very soluble, the solution being a good conductor of the electric current. When the excess of methylamine is allowed to escape at room temperature the product assumes a constant weight but remains a viscous liquid, resisting all attempts to induce crystallization.

0.1608 gram pyrogallol retains 0.1135 gram of methylamine.

$C_6H_3(ONH_3CH_3)_3$, calculated CH_3NH_2 42.52 per cent., found 41.4.

Upon exhaustion with the water pump the substance quickly gives up methylamine and assumes the solid state and practically constant weight.

0.1608 gram of pyrogallol retains 0.0763 gram of methylamine.

$C_6H_3.OH.(ONH_3CH_3)_2$, calculated CH_3NH_2 33.02 per cent., found 32.2.

With the mercury pump the compound gives up an additional very small amount of methylamine, the stable form evidently being that in which two molecules of methylamine are in combination with one of pyrogallol. This compound is very soluble in water and on contact with the oxygen of the air is at once darkened in a manner characteristic of an alkaline solution of pyrogallol. An ammonia compound, $C_6H_3(OH)_2.ONH_4$, has been prepared by passing dry ammonia gas into a solution of pyrogallol in dry ether.[2]

Phenolphthalein is very soluble, the resulting solution being of a faint pink color and a fair conductor of the electric current. If all traces of moisture are absent from the methylamine and the phenolphthalein, the solution will in all probability be without color. Upon the removal of the excess of methylamine a viscous mass is first formed from which no crystals were induced to grow, and with the mercury pump this dried to a white solid.

0.0854 gram of phenolphthalein retains 0.0160 gram of methylamine.

$C_6H_4C_2O_2(C_6H_4.ONH_3CH_3)_2$, calculated CH_3NH_2 16.3 per cent., found 15.79.

[1] Malin: Ann. 138, 80; Baker: Patentschrift des Deutschen Reiches, 40372; Friedländer's "Fortschritte der Theerfarbenfabrication," 1, 564.

[2] Luynes and Esperandien: Ann. Supplement, 6, 252.

The compound dissolves in water, giving a red solution. From previous considerations of the behavior of the hydroxyl ring compounds at ordinary temperatures and below, in the absence of water, it seems quite probable that the methylammonium salt of phenolphthalein is formed. Baeyer[1] has found that a solution of phenolphthalein in aqueous ammonia loses all of its ammonia on drying, while on heating in sealed tubes at 160° to 170° iminophenolphthalein,[2] $C\begin{cases}:(C_6H_4OH)_2\\.C_6H_4.C(NH)\\.NH\end{cases}$, is produced. H. Meyer,[3] by the action of ammonia solutions at about the same temperatures, obtained monoiminophenolphthalein, $C\begin{cases}:(C_6H_4OH)_2\\.C_6H_4CO\\.NH\end{cases}$, as the principal product. In both cases the hydroxyl group remains intact.

Alizarin turns a dark purple immediately on contact with the vapor of methylamine, a perceptible rise of temperature resulting. When liquid methylamine is poured upon the crystals they turn a brilliant dark blue and dissolve, forming an intense purple solution which conducts the electric current to some extent. After the removal of the excess of methylamine by spontaneous evaporation under slightly reduced pressure a solid of a dark red-brown color remains.

0.1091 gram of alizarin retains 0.0286 gram of methylamine. $C_6H_4.C_2O_2.C_6H_2(ONH_3CH_3)_2$, calculated CH_3NH_2 20.6 per cent., found 20.8.

This compound is extremely soluble in water, giving a purple-red solution. No attempt was made to prepare the compound containing one less molecule of methylamine, $C_6H_4.C_2O_2.C_6H_2OH.ONH_3CH_3$, by exhaustion with the mercury pump, but it seems quite probable from the results obtained with quinol and resorcinol that this compound can be obtained. It is probable that the ammonium salt, $C_{14}H_7O_4.NH_4$, has been prepared by Perkin,[4] although no analyses of the compound were made.

[1] Ann. 204, 74.
[2] Baeyer and Burkhardt: Ber. 11, 2297; Ann. 204, 111.
[3] Monatsh. 20, 358.
[4] J. Chem. Soc. 75, 435.

THE ALDEHYDES.

Acetic aldehyde is readily miscible with violent rise of temperature and the discoloration of the liquid. The solution is a fair conductor of the electric current. No reaction products have been isolated.

Benzaldehyde is readily miscible with strong rise of temperature. The solution formed is a fairly good conductor of the electric current, due probably to the presence of benzoic acid. Upon distilling off the methylamine, by cooling one leg of the reaction tube in liquid ammonia, the conductivity of the solution rapidly decreases. When the two liquids are again mixed, the temperature again rises and the conductivity returns to the previous figure. After removing the excess of methylamine with the mercury pump and cooling the resulting liquid in liquid ammonia, colorless crystals form very slowly. The composition of the reaction products has not been determined.

Metanitrobenzaldehyde is readily soluble with slight rise of temperature. The resulting pink solution is a poor conductor of the electric current. On cooling the solution in liquid ammonia beautiful dark red crystals can be induced to grow. When the excess of methylamine is allowed to escape, the entire solution can be made to solidify into a mass of these crystals which melt quite sharply at —9.0°.

0.1890 gram metanitrobenzaldehyde retains 0.2439 gram of methylamine.

$C_6H_4.NO_2CHO.6CH_3NH_2$, calculated CH_3NH_2 55.24 per cent., found 56.3.

Upon exhausting the tube with the mercury pump, another crop of crystals is obtained. These are lighter in color, melt at about 47°, at which temperature they also undergo decomposition.

0.1890 gram metanitrobenzaldehyde retains 0.0422 gram of methylamine.

$C_6H_4.NO_2CHO.CH_3NH_2$, calculated CH_3NH_2 17.1 per cent., found 18.3.

There is some evidence of an intermediate product lying between the two described.

THE KETONES AND QUINONES.

Acetone is miscible in all proportions and the solution which is formed is to some extent a conductor of the electric current.

The conductivity, however, may be due to the dissociation of the methylamine in the acetone. The evidence of a reaction taking place between the two liquids when in contact for several hours, was very slight.

Götschmann[1] has obtained, by combination of acetone and methylamine on long standing, methyldiacetonamine, $CH_3.CO.CH_2C(CH_3)_2.NH(CH_3)$. The action of aniline upon acetone in sealed tubes has been studied by Pauly.[2]

Benzophenone is quite soluble and readily crystallizable unchanged from the solution, which is a very poor conductor of the electric current.

The action of ammonia upon benzophenone in sealed tubes has been studied by Pauly.[3]

Benzil is very soluble with marked rise of temperature. The solution which is formed is a poor conductor of the electric current. Upon the removal of the excess of methylamine a mass of poorly defined yellow crystals is formed which melt at about 23°. These do not give methylamine on boiling with potassium hydroxide solution.

0.2620 gram benzil gained 0.0674 gram in weight.

$(C_6H_5)_2(CO)_2.2CH_3NH_2$, calculated CH_3NH_2 20.46, found 22.4.

The reaction which takes place is probably deep-seated. Laurent[4] and others described complicated reactions corresponding to this in ammonia solutions.

Carbamide is very soluble without reaction. The compound is readily crystallizable unchanged from the solution, which is a poor conductor of the electric current.

Quinone reacts immediately on coming in contact with the vapors of methylamine, turning successively green, purple and black, with evolution of much heat. The solution is of a dark red color and is a fairly good conductor of the electric current. A study of the reaction products has not yet been attempted.

By action of dry ammonia in alcohol, ether and chloroform solutions, various products have been produced.[5] The action of some substituted ammonias with quinone and substitution prod-

[1] Ann. 197, 38.

[2] Ibid. 187, 216.

[3] Loc. cit.

[4] J. pr. Chem. 35, 461; Henius: Ann. 228, 341; Pinner: Ber. 35, 4138.

[5] Waskresensky: Jsb. 26, 801; J. pr. Chem. 34, 251; Knapp and Schultz: Ann. 210, 178; Hebebrand and Zinke: Ber. 16, 1555.

ucts of quinone has also been investigated. By heating quinone with dimethylamine solution tetramethyldiaminoquinone is obtained,[1] $(N(CH_3)_2)_2C_6H_2O_2$.

Anthraquinone is only slightly soluble with no evidence of reaction and the solution is practically a non-conductor of the electric current.

THE ACIDS.

Acetic acid is very soluble with strong rise of temperature. The colorless solution which is formed is a good conductor of the electric current. By cooling the solution beautiful colorless crystals which evidently contain some methylamine of crystallization are obtained. At atmospheric pressure they give up methylamine, forming methylammonium acetate which melts at about 80°. This salt is very soluble in water and the solution is a good conductor of the electric current

0.4050 gram acetic acid unites with 0.2091 gram of methylamine.

$CH_3COO.NH_3CH_3$, calculated CH_3NH_2 34.11, found 34.03.

On heating the methylammonium acetate above the melting-point in sealed tubes a reaction takes place, probably producing methylacetamide, $CH_3CO.NHCH_3$,[2] although the compound was not isolated.

Phenylacetic acid behaves in a manner very similar to acetic acid. It is very soluble with strong rise of temperature and the solution is a good conductor of the electric current. From this solution on cooling, beautiful crystals which evidently contain methylamine of crystallization, are obtained. They immediately lose their form upon release of the pressure and give up methylamine, forming methylammonium phenyl acetate.

0.2300 gram phenylacetic acid unites with 0.0545 gram methylamine.

$C_6H_5.CH_2COO.NH_3CH_3$, calculated CH_3NH_2 18.57, found 19.1.

This salt is very soluble in water and the solution is a good conductor of the electric current.

Beilstein gives no record of the ammonium salt or the methylammonium salt, but the amide $C_6H_5.CH_2CO.NH.CH_3$ has been prepared.[3]

[1] Kehrmann: Ber. 23, 905; Mylius: Ibid. 18, 467.

[2] Prepared previously by Hofmann: Ber. 14, 2729; Franchimont: Rec. trav. chim. 2, 121.

[3] Ergänzungsb. II, 814 (1903).

Palmitic acid is very soluble and the solution is a fair conductor of the electric current.

0.1140 gram palmitic acid unites with 0.0136 gram methylamine.

$C_{15}H_{31}COO.NH_3CH_3$, calculated CH_3NH_2 10.81, found 10.66.

This salt melts at about the same temperature as palmitic acid, namely 62°, is quite soluble in water and is decomposed by caustic potash solution.

Succinic acid reacts immediately on contact with methylamine with evolution of much heat. The reaction products are insoluble in the liquid.

0.6207 gram succinic acid unites with 0.3290 gram of methylamine.

$C_2H_4(COONH_3CH_3)_2$, calculated CH_3NH_2 34.12, found 34.6.

The methylammonium succinate is very hygroscopic, begins to decompose at 130° and gradually assumes a quiet state of fusion at 150°. On cooling, the liquid solidifies to a mass of colorless crystals. The composition of this crystalline substance was not determined.

Methylsuccinimide has been prepared by Menschutkin[1] by the distillation of the salt of succinic acid and methylamine.

Tartaric acid (*d*) reacts immediately on contact with methylamine with the evolution of much heat. The reaction products are insoluble in the liquid.

0.8328 gram tartaric acid unites with 0.3474 gram of methylamine.

$C_2H_2(OH)_2(COONH_3CH_3)_2$, calculated CH_3NH_2 29.19, found 29.43.

The methylammonium tartrate melts, probably with decomposition, at about 148°. It is so very hygroscopic that the salt is soluble in the smallest amount of water and cannot be again dried in a vacuum desiccator over sulphuric acid. Methylamine bitartrate is described by A. Ladenburg[2] as melting and decomposing at 170° with the production of two stereoisomeric methyl tartrimides. The racemic variety was also prepared by Wende.[3]

Benzoic acid is very soluble with rise of temperature. The solution is a very good conductor of the electric current. Upon

[1] Ann. 182, 92.

[2] Ber. 29, 2710.

[3] Ibid. 29, 2719.

removing the excess of methylamine with the mercury pump a white solid is obtained.

1. 0.3487 gram of benzoic acid unites with 0.0803 gram methylamine.

2. 0.5320 gram of benzoic acid unites with 0.1452 gram methylamine.

$C_6H_5.COO.NH_3CH_3$, calculated CH_3NH_2 20.27, found I, 18.7; II, 20.9.

The methylammonium benzoate is a very hygroscopic white solid, very soluble in methyl alcohol, ethyl alcohol and insoluble in ether. It is decomposed on heating at atmospheric pressure into benzoic acid and methylamine. Heated in a sealed tube it melts at 110–112°. The affinity for water is so great that the wet salt cannot be dried in a vacuum desiccator over sulphuric acid.

Methylbenzamide, $C_6H_5.CO.NH.CH_3$, has been prepared but not from methylammonium benzoate.[1]

Orthonitrobenzoic acid is very soluble with rise of temperature. The solution is a good conductor of the electric current. When the temperature of the reacting substances is allowed to rise it is quite probable that the nitro group also enters into the reaction. When the temperature is maintained at a low point only the carboxyl group reacts with the methylamine, forming the methylammonium salt. This salt crystallizes from the concentrated solution in beautiful pale yellow needles.

0.7460 gram of orthonitrobenzoic acid retains on the mercury pump 0.1420 gram of methylamine.

$C_6H_4.NO_2.COONH_3CH_3$, calculated CH_3NH_2 16.69, found 16.0.

These crystals are very soluble in water, methyl alcohol, ethyl alcohol and insoluble in ether. They can be crystallized readily from a mixture of alcohol and ether. Without further purification they melt from 128° to 129°.

Phthalic acid forms methylammonium phthalate upon contact with methylamine. The salt is insoluble in the liquid, very soluble in water, from which solvent it crystallizes in beautiful colorless crystals which decompose easily upon heating.

0.3535 gram of phthalic acid unites with 0.1446 gram of methylamine.

$C_6H_4.(COO.NH_3CH_3)_2$, calculated CH_3NH_2 27.2, found 29.0.

[1] Beilstein: 2, 1159 (1896).

Phthalic anhydride reacts with the production of much heat and the resulting compound is insoluble in the liquid.

0.2122 gram of phthalic anhydride retains 0.0855 gram of methylamine.

$C_6H_4\begin{cases}COONH_3CH_3\\CONHCH_3\end{cases}$, calculated CH_3NH_2 27.5, found 28.7.

The methylammonium methylphthalamate, which probably is produced, is very soluble in water and from the solution beautiful, colorless, transparent, star-shaped crystals slowly form.

Methylphthalimide,[1] $C_6H_4(CO)_2NCH_3$, has been prepared from phthalic anhydride and methylamine.

Uric acid reacts with methylamine and the product, a white powder, is insoluble in the liquid.

0.1354 gram uric acid combines with 0.0225 gram methylamine.

$C_5H_4N_4O_3.CH_3NH_2$, calculated CH_3NH_2 15.5, found 14.2.

The methylammonium urate is soluble in warm water and decomposes on heating without melting. The methylamine in combination was determined by distillation with caustic potash, the distillate collected in N/10 hydrochloric acid.

0.0919 gram methylammonium urate required 4.15 cc. acid to neutralize the distillate. This is equivalent to 14.03 per cent. of methylamine.

Hippuric acid is very soluble with slight rise of temperature. The solution is a good conductor of the electric current. As the excess of methylamine escapes, crystals of methylammonium hippurate are formed.

0.3341 gram of hippuric acid unites with 0.0564 gram methylamine.

$C_6H_5.CO.NHCH_2COONH_3CH_3$, calculated CH_3NH_2 14.7, found 14.4.

The salt is very soluble in cold water and the solution is a good conductor of the electric current.

THE HALOGEN SUBSTITUTION PRODUCTS.

Chloroform is miscible in all proportions and a reaction gradually sets in between the two liquids in the cold. The conductivity of the solution slowly increases as the reaction proceeds. At higher temperatures it is very probable that the reaction will be

[1] Graebe and Pictet: Ann. 247, 302.

more rapid. On spontaneous evaporation of the solution on a watch-glass the isocyanide odor is very marked. A very hygroscopic residue remains which becomes crystalline on standing in a vacuum desiccator over sulphuric acid. These crystals are probably methylammonium chloride, for they decompose with caustic potash, giving the odor of methylamine and with silver nitrate show the presence of the chlorine ion. The most probable reaction is $CHCl_3+CH_3NH_2=CH_3NC+3HCl$, the hydrochloric acid uniting with methylamine to produce methylammonium chloride.

Ethylene bromide is miscible but not in all proportions. A reaction slowly commences and becomes very violent unless the reaction tube is kept in a cooling mixture. The products are soluble in liquid methylamine and the solution is a very good conductor of the electric current. From the concentrated solution a mass of beautiful colorless crystals, resembling the cubical crystals of sodium chloride, is obtained on cooling. They are found to be extremely hygroscopic and cannot be recrystallized from aqueous solution. They are insoluble in dry ether and are purified by repeated washing with this solvent and drying with the mercury pump. During the washing, which is conducted in the reaction tube, all air must be excluded, for traces of moisture are sufficient to spoil the form of the beautiful crystals. The melting-point, 179°, is not as sharp as might be desired.

0.9052 gram of substance was dissolved in 200 cc. of water and aliquot parts taken for analysis. The base was set free with caustic potash solution and collected by distillation. The bromine was determined by precipitating and weighing as silver bromide.

I. 1/10 of 0.9052 gram required 7.12 cc. N/10 hydrochloric acid.

II. 1/10 of 0.9052 gram required 7.14 cc. N/10 hydrochloric acid.

Calculated for $(CH_2.NH.CH_3HBr)_2$: Br, 63.91. Found: Br, 64.27 and 64.37.

Calculated for $(CH_2NH.CH_3HBr)_2$: $(CH_2.NH.CH_3)_2$, 35.26. Found: $(CH_2NH.CH_3)_2$, 34.68 and 34.78.

The reaction which takes place is probably best represented by the equation:

$$\begin{array}{lll} CH_2Br & CH_3NHH & CH_2.NH.CH_3.HBr \\ | & + & = | \\ CH_2Br & CH_3NHH & CH_2.NH.CH_3.HBr \end{array}$$

(Ethylenedimethyldiamine hydrobromide.)

The hydrochloride of this base has been prepared by Schneider[1] by heating dimethylethylenedibenzenesulphamide with hydrochloric acid. He states the boiling-point of the base to be 119°, and the melting-point of the hydrochloride to be 235–236°.

Brombenzene is miscible and the solution is a non-conductor of the electric current. If any reaction takes place, it goes on so slowly, at room temperature and below, as to be imperceptible. The brombenzene can be separated unchanged by distilling off the methylamine.

Parabromacetanilide is very soluble without reaction and separates unchanged from the concentrated solution, which is a poor conductor of the electric current.

THE NITRO COMPOUNDS.

Nitromethane is miscible, a slight rise of temperature resulting. The solution is a fairly good conductor of the electric current. On cooling in liquid ammonia colorless crystals are formed. By blowing off the mother-liquor, melting the crystals and recrystallizing seven different times they melt quite sharply from —8.0° to —7.5°. Analysis was made by distilling with potassium hydroxide and collecting the distillate in N/10 hydrochloric acid.

0.5439 gram of substance gave 0.2050 gram of methylamine.

$CH_3NO_2.CH_3NH_2$, calculated CH_3NH_2 33.7, found 37.8.

It would be expected from this method of production that the crystals would be contaminated by some free methylamine.

Nitrobenzene is miscible, producing an intense dark red solution, with a slight rise of temperature. The solution is to a small extent a conductor of the electric current. In all probability no reaction takes place at the temperatures studied.

Metadinitrobenzene is very soluble. Immediately upon contact with methylamine vapor the compound turns a beautiful purple and as the solvent distils into the tube a brilliant, reddish purple solution is formed. The solution is a good conductor of the electric current. On concentrating the solution, crystals of metadinitrobenzene separate out and these resume their original color as the methylamine evaporates. There is no evidence of a

[1] Ber. 28, 3072.

reaction. The brilliantly colored solution is in all probability due to dissociation in the electrolytic solvent.

The behavior of dinitrobenzene in liquid ammonia is somewhat analogous and has been studied by Franklin and Kraus.[1]

*Orthonitrotoluene** is very soluble. The solution is slightly yellow.

*Dinitrotoluene** (2-4) is very soluble. The solution is blue in color, greenish in thin layers.

Dinitraniline (1-2-4) is not affected by the methylamine vapor but in the liquid the crystals immediately turn a brilliant red and quickly go into solution. The brilliant red solution is a good conductor of the electric current. The original substance crystallized unchanged from the solution.

Trinitraniline (1-2-4-6) melts on contact with the vapor of methylamine with evolution of heat and formation of a dark red mass. The dark red solution which is formed is a good conductor of the electric current. From the concentrated solution, brilliant red crystals are formed. The reaction which evidently goes on has not been further investigated.

THE SUGARS.

Galactose is quite soluble, a slight rise of temperature resulting. The solution is a poor conductor of the electric current. Upon the removal of the excess of methylamine a viscous mass, which becomes solid on standing, results.

0.2440 gram galactose retains with the mercury pump at good vacuum 0.0775 gram of methylamine.

$C_5H_{11}O_5CHO.2CH_3NH_2$, calculated CH_3NH_2 25.3, found 24.1.

The reaction products have not been investigated.

Glucose behaves in a manner quite analogous to galactose; however, the viscous mass obtained after removal of the methylamine, crystallizes quite well on standing.

0.4520 gram of glucose retains on the mercury pump 0.1023 gram of methylamine.

$C_5H_{11}O_5CHO.2CH_3NH_2$(?), calculated CH_3NH_2 25.3, found 18.4.

The reaction products have not been investigated.

Sucrose is quite soluble, a slight rise of temperature resulting. The solution is to a slight extent a conductor of the electric current. There is some evidence of a reaction but the question has not been sufficiently investigated.

[1] Loc. cit.

MISCELLANEOUS COMPOUNDS.

Acetamide is very soluble without reaction. From the solution, which is a fairly good conductor of the electric current, the compound is readily crystallizable.

Phenylhdyrazine is miscible in all proportions and there is no evidence of a reaction. The solution is to some extent a conductor of the electric current.

Amyl formate is miscible in all proportions. The sample employed was evidently contaminated with a small amount of formic acid and therefore no definite conclusions can be drawn as to the conductivity of the solution.

Pyridine is miscible in all proportions without reaction. The solution is a non-conductor of the electric current.

Azobenzene is very soluble. From the brilliant red solution, which is a non-conductor of the electric current, the azobenzene crystallizes beautifully. There is no evidence of a reaction.

Diphenylketoxime dissolves almost immediately on contact with the vapors of methylamine, a slight rise of temperature resulting. The solution is to a small extent a conductor of the electric current. The more dilute solutions seem to be better conductors than the concentrated. From the concentrated solution beautiful colorless crystals are obtained.

0.5246 gram diphenylketoxime retains with the mercury pump at good vacuum 0.0850 gram of methylamine.

$(C_6H_5)_2CNOH.CH_3NH_2$, calculated CH_3NH_2 13.62, found 13.94.

This compound decomposes a few degrees below 140°, giving off methylamine and leaving the oxime which melts at 140°. A further study of the composition of the compound was not made.

Benzenesulphimide is very soluble with reaction. The resulting solution is a good conductor of the electric current. On the removal of the excess of methylamine on the mercury pump only a semi-solid mass results, from which no crystals are obtained. The reaction was not further studied.

Metanitrobenzenesulphonamide is quite soluble and the colorless solution is a good conductor of the electric current.

DYES.

Gallein turns a brilliant blue immediately upon contact with methylamine vapor, a strong rise of temperature resulting. The reaction products are only slightly soluble in the liquid, pro-

ducing a bluish purple solution which is a poor conductor of the electric current. Upon removal of the excess of methylamine with the mercury pump 0.2891 gram of gallein holds 0.0814 gram of methylamine.

$C_{20}H_{12}O_7.3CH_3NH_2$, calculated CH_3NH_2 20.5, found 21.7.

The resulting solid is, by reflected light, a very dark purple.

It is evident that the carboxyl group will unite with one molecule of methylamine, and, judging from the behavior of other hydroxyl ring compounds such as phenol, quinol, resorcinol and pyrogallol, when two hydroxyl groups are united to the same ring only one uniting with methylamine to form a stable compound, a second molecule of methylamine is accounted for by combination with the ring holding the two hydroxyl groups. The third molecule can easily be held by the hydroxyl group or the quinone oxygen of the other ring as both have been found to be reactive. The reaction products, have, however, not been investigated in order to verify this theory.

Coerulein is very soluble, a slight rise of temperature resulting. The dark green solution which is formed is a poor conductor of the electric current.

0.1635 gram of coerulein retains with the mercury pump 0.0272 gram of methylamine.

$C_{20}H_{10}O_6.2CH_3.NH_2$, calculated CH_3NH_2 15.2, found 14.8.

The resulting solid is, by reflected light, a very dark green.

The arguments used in the case of gallein concerning the character of the reaction, hold equally well here.

Dichlorgallein turns a brilliant blue immediately upon contact with methylamine vapor. The brilliant blue solution which is formed with the liquid is a very poor conductor of the electric current. The reaction which takes place is more complicated than the reaction between methylamine and gallein. The product which holds about 23 per cent. methylamine has not been investigated.

Tetrachlorgallein[1] turns a brilliant blue immediately on contact with the vapor of methylamine, a perceptible rise of temperature resulting. The reaction products, which are only slightly soluble

[1] My thanks are due to Professor William R. Orndorff, of Cornell University, for the samples of gallein, coerulein, dichlorgallein and tetrachlorgallein, which are the same as those employed by Orndorff and Brewer in their investigation of the constitution of these compounds. Am. Ch. J. 26, 97.

in liquid methylamine, form a blue solution which is a poor conductor of the electric current. The reaction product holds over 25 per cent. of methylamine, is very soluble in water and does not contain the chlorine ion. No further study of the reaction has been made.

Indigo is very soluble, a slight rise of temperature resulting. The dark green solution which is formed is a good conductor of the electric current. There is no evidence of a reaction, for the indigo separates unchanged from the concentrated solution.

Methyl orange is to a small extent soluble. The resulting deep red solution is a moderately good conductor of the electric current. There is no evidence of a reaction as the original substance separates unchanged upon opening the reaction tube and allowing the methylamine to escape.

Rosaniline turns a dirty brown color immediately on contact with the vapors of methylamine, a slight rise of temperature resulting. This compound is very soluble in the liquid and the resulting dirty brown solution is to a slight extent a conductor of the electric current.

INORGANIC COMPOUNDS.

The solubilities of a number of inorganic compounds have been investigated by Franklin[1] but the reactions which occur in many cases have been investigated in only a few instances. For the most part the sulphates of the metals are insoluble in liquid methylamine, while the nitrates and the halogen salts are about equally divided.

*Aluminum chloride** is insoluble.

*Arsenious iodide** is very soluble.

*Ammonium chloride** is very soluble.

*Bismuth nitrate** is insoluble.

*Bismuth chloride** is very soluble with the separation of a white mass. Probably a basic salt analogous to Franklin's ammono basic salts[2] is formed.

*Boric acid** is slightly soluble with slow reaction, producing an amorphous mass which is presumably the methylammonium salt.

[1] All of the data on the inorganic compounds, with the exception of silver nitrate, methyl mercuric chloride, mercuric cyanide, mercuric chloride, mercurous chloride and mercuric iodide, have been taken from his unpublished notes.

[2] This Journal, 27, 826.

*Cadmium iodide** unites with methylamine to form a bulky, white mass which is insoluble, or only slightly soluble in the liquid.

0.1096 gram of cadmium iodide unites with 0.0369 gram of methylamine.

$CdI_2.4CH_3NH_2$, calculated CH_3NH_2 25.31, found 25.26.

*Calcium chloride** unites with methylamine, forming a bulky mass which is insoluble.

*Cuprous chloride** reacts, producing an unpromising mass which was not investigated.

*Cupric sulphate** forms an intensely blue mass which is insoluble.

*Chromic chloride** is slightly soluble, forming with an excess of the solvent a purple mass which is an addition product.

*Iodic acid** is insoluble.

*Lithium chloride** is very soluble, forming a viscous solution which solidifies to a crystalline mass on cooling.

*Lithium nitrate** is very soluble. On standing, the contents of the tube solidify to a crystalline mass.

*Lead nitrate** forms a bulky addition product with the evolution of heat.

Mercuric chloride unites with the solvent with evolution of heat and the formation of a white addition product which is only slightly soluble in the liquid. The solution is a poor conductor of the electric current.

Mercurous chloride blackens in the methylamine and a mass of crystals separates out on cooling.

Methyl mercuric chloride is quite soluble at room temperature but on cooling crystals separate out, the solution almost completely solidifying. The solution is a very good conductor of the electric current.

Mercuric cyanide is very soluble with evolution of heat. The colorless solution which is formed is a fair conductor of the electric current. On cooling, crystals are formed in the solution.

Mercuric iodide is very soluble. The colorless solution which is formed is a very good conductor of the electric current. An addition product, $HgI_2.XCH_3NH_2$, crystallizes out as a white solid on cooling. Composition not determined.

*Mercurous nitrate** blackens on contact with the liquid and goes into solution.

Potassium bromide,* *chlorate** *and chromate** are insoluble.

*Potassium permanganate** is very soluble.

Silver nitrate is extremely soluble with considerable rise of temperature. There is at first a blackening of the silver nitrate, and fine black particles are seen suspended in the liquid. These disappear as the concentration decreases, the liquid becoming clear and colorless. The colorless solution which is formed is an excellent conductor of the electric current. When the excess of methylamine is allowed to escape upon opening the stop-cock, a heavy viscous liquid results. Upon cooling this liquid it completely solidifies to a mass of colorless needle crystals which melt at about the temperature of the room.

0.9005 gram of silver nitrate crystallizes with 0.6283 gram of methylamine.

$AgNO_3.4CH_3NH_2$, calculated CH_3NH_2 42.2, found 41.1.

When the pressure is reduced, these crystals immediately lose their form, giving up methylamine and turning green in color. When the vacuum is fairly good with the mercury pump there still remains held 0.3704 gram of methylamine.

$AgNO_3.2CH_3NH_2$, calculated CH_3NH_2 26.8, found 29.1.

This substance upon standing continues to give up methylamine. Under the microscope it is seen to have a crystalline structure, the crystals being of a green color or contaminated by impurities which give them the green cast. The crystals are decomposed by water, going partially into solution and leaving a dark brown residue which is soluble in ammonia solution. The crystals are soluble in potassium cyanide solution, insoluble in dry ether and quite soluble in absolute alcohol. On heating they fuse and then explode, giving the isocyanide odor very strongly and leaving a residue of metallic silver.

*Silver sulphate** is insoluble.

*Sodium nitrate** is very soluble.

*Sodium sulphite** is insoluble.

*Sodium thiosulphate** reacts with the solvent.

*Tetramethylammonium iodide** is insoluble.

*Thallium chloride** is insoluble.

SUMMARY.

Liquid methylamine has been found to be a remarkably good solvent for organic compounds, exceeding liquid ammonia and

perhaps exceeding methyl alcohol,[1] while for inorganic compounds it is not as good a solvent as liquid ammonia, far inferior to water and ranking perhaps closer to methyl alcohol. It is extremely reactive with both organic and inorganic compounds, in this respect, probably, exceeding the most reactive of the other three solvents mentioned, namely liquid ammonia.[2]

Next to its wide solvent action the most striking property of liquid methylamine is its remarkable power of uniting with many compounds, both organic and inorganic as methylamine of crystallization. Among those mentioned in the literature are: $LiCl.CH_3NH_2$;[3] $LiCl.2CH_3NH_2$;[3] $LiCl.3CH_3NH_2$;[3] $LiCl.4CH_3NH_2$;[4] $ZrCl_4.4CH_3NH_2$;[5] $ThCl_4.4CH_3NH_2$;[5] $PbCl_4.4CH_3NH_2$;[5] $AgCl.CH_3NH_2$;[6] $AgBr.CH_3NH_2$;[6] $AgI.CH_3NH_2$;[6] $2AgI.CH_3NH_2$;[6] $CH_3NH_2.H_2O$;[7] and $C_6H_2(NO_2)_3.OH.CH_3NH_2$.[8]

Addition products other than those already described in the literature, which in all probability contain methylamine of crystallization, have been prepared from phenol, quinol, resorcinol, α-naphthol, β-naphthol (?), metanitrobenzaldehyde, galactose (?), acetic acid, phenylacetic acid, diphenyl ketoxime, nitromethane, bismuth chloride, cadmium iodide, calcium chloride, cuprous chloride (?), cupric sulphate (?), chromic chloride, lithium chloride, lithium nitrate, lead nitrate, mercuric chloride, mercurous chloride (?), methyl mercuric chloride, mercuric cyanide (?), mercuric iodide and silver nitrate.

This work was commenced at Stanford University at the suggestion of Professor E. C. Franklin, and carried to its present state of completion under his kindly advice, direction and assis-

[1] Liquid methylamine probably does not exceed liquid ammonia as a solvent for organic compounds to the same extent as methyl alcohol exceeds water for the same purpose.

[2] This has often been observed in the case of aqueous and alcoholic solution of ammonia and methylamine. Lassar-Cohn, "Applications of Some General Organic Reactions," page 36. Laubenheimer: Ber. 11, 1155; A. Hempel: J. pr. Chem. [2] 41, 161; Kehrmann and Messinger: Ibid. [2] 46, 565; Bettenhausen-Marquardt, Schulz, Patentschrift des Deutschen Reiches, 72, 253; Paal and Sprenger: Ber. 30, 62; Ristenpart: Ibid. 29, 2526.

[3] Bonnefoi: Compt. rend. 127, 516.

[4] Ibid. 124, 771.

[5] Matthews: This Journal, 20, 826.

[6] Jarry: Compt. rend. 124, 964; Ann. chim. phys. [7] 17, 376.

[7] Henry: Private paper; Beilstein: Ergänzungsb. 1, 596.

[8] Delépine: Ann. chim. phys. [7], 8, 461.

tance. I am grateful to him for the many favors shown me. The manuscript was in process of preparation at the time of the San Francisco fire, and a small portion of the work cannot be chronicled here, owing to the destruction of the notes. As opportunity offers, the research will be extended.

FOOD LABORATORY OF THE
SAN FRANCISCO HEALTH COMMISSION,
May 15, 1906.

[CONTRIBUTION FROM THE COMMITTEE ON PURITY OF REAGENTS, No. 1.]

SOME SOURCES OF IMPURITIES IN C. P. CHEMICALS.[1]

BY J. W. SCHADE.

Received June 30, 1906.

THE elimination of impurities in chemically pure chemicals has long been the desire of chemists; but owing to a seeming indifference on their part, the manufacturers have not exerted themselves to make their products better than they deemed absolutely necessary to meet the demands. During the past year or two much increased interest has been manifested in the movement to secure the best grade of laboratory reagents consistent with economy in manufacture. To ask for a reagent "absolutely pure" is to ask, in most cases, for the impossible in economical manufacture. The object of this paper is to present some sources of impurities in chemical reagents and to point out that there are limits of purity obtainable by manufacturers.

With few exceptions all reagents are shipped in glass containers. The dry salts probably do not take up impurities from the bottles, but acids and ammonia after standing in containers for a few days are contaminated with impurities from the glass. These impurities may be one or more of the following: iron, potassium, sodium, silica, calcium and from bottles of Jena or "Nonsol" glass, zinc. In the case of ammonia, silica is the principal impurity from the glass; in the case of acids, iron. The latter is due mainly to the fact that small chips of iron oxide flake from the blowpipes used by the glassblowers and although acid is allowed to stand in the bottles before they are washed for use, there are undoubtedly minute particles that escape immediate solution. Acids shipped in carboys having glass covers secured by zinc rings are liable to contamination from the zinc, owing to the

[1] Read at the Ithaca Meeting of the American Chemical Society.

splashing of the acid into the neck of the carboy. Hydrofluoric acid shipped in lead carboys takes up that metal as an impurity. The nature of these impurities is such that the liability of contamination cannot be entirely removed, though it may be diminished by the use of more resistant glass and of glass stoppered carboys.

The second source of impurities is in the chemical works. It is the vessels in which the chemicals are manufactured. These vessels—tanks, stills, condensers, crystallizing dishes, and so on—are made or lined with lead, silver, copper, iron, aluminum, nickel, zinc, platinum, porcelain, earthenware, or glass. The impurities from this source are the metals of which the vessels are made, and from the non-metallic receptacles silica, sodium, potassium, calcium and iron. Iron vessels give rise to other impurities than iron, notably manganese. In the manufacture of sodium bismuthate, for instance, iron vessels cannot be used, owing to the contamination of the product with manganese which, of course, is inadmissible in that reagent. Nickel is found in the best grades of caustic alkalies from the dishes in which they are made. Copper, aluminum, or silica are found in acetic acid from the condensers used in the distillation. Lead tanks are very generally used, especially for crystallizing organic acids such as tartaric and citric. The author has also found it in hydrofluoric acid, ammonium chloride, potassium sulphate, and sodium chloride. The amount of impurities of this class is minimized by the judicious selection of vessels to meet the needs of each case. As with the first class, however, the liability to contamination cannot be entirely removed.

There is another class of impurities introduced during the purification of the salts. These impurities are reagents used to precipitate certain foreign substances or the salts formed by the reaction. For instance, the author once analyzed a sample of sodium chloride in which sulphate had been precipitated by means of barium chloride. This salt gave decided tests for both barium and sulphate, an anomalous condition often met in testing reagents. Another example of this is the presence of calcium in ammonium oxalate. Samples of ammonium oxalate giving clear solutions sometimes contain some hundredths of a per cent. of calcium though the solution from which the crystals were obtained was alkaline. It is evident from these facts that the so-

called "insoluble precipitates" are dissolved to an appreciable extent by the concentrated solutions from which the salts are crystallized.

The final class of impurities includes those occurring in the original source of the chemicals, *i. e.*, in the minerals, and in those substances used in manufacture. These impurities will vary in number and kind, depending on whether the treatment of the mineral is simple or complicated. Sometimes it is impossible for the manufacturer to get rid of certain impurities without putting a prohibitive price on an article. Iron, alumina, and silica, appear in all but the highest-priced grades of caustic alkalies and alkali carbonates. Nickel and cobalt cannot be entirely separated on the large scale cheaply. As has been pointed out above, calcium cannot be entirely removed from ammonium oxalate, strange as it may seem, without considerable trouble and expense. Again, strontium sulphate will not precipitate barium from a solution of strontium chloride or nitrate unless a large excess is added, in which case sulphate is introduced as an impurity. Here the manufacturer is compelled to choose the lesser of two evils. This is the inevitable alternative in many instances.

Calcium persists in barium salts and if considerable calcium is present in the mineral from which the barium is obtained, it is no easy matter to remove it. The removal of iron from copper sulphate is not as simple as one would imagine. Some of the "iron-free" copper sulphate sold on the market contains several thousandths of a per cent. of iron. To separate the two iron must be in the ferric condition. Hydrogen peroxide is theoretically an ideal oxidizing agent in that it introduces no impurity into the copper sulphate, but in practice, nitric acid works somewhat better. Here is a case in which nitric acid is introduced as an impurity in preference to iron. Lead is sometimes found in copper salts and is difficult to remove from the chloride and nitrate. Ferric salts always contain free acid, fused magnesium chloride always contains ammonia, and caustic alkalies and alkali carbonates, as has been said, almost always contain iron, alumina and silica.

These illustrations serve to show that at ordinary prices chemical reagents must be limited in purity. This, however, is not a serious difficulty except in cases when extraordinarily accurate work is to be performed; and the manufacturer can supply at a reasonable

price reagents that will give accurate results when put to the ordinary uses.

LABORATORY OF THE J. T. BAKER CHEMICAL CO.,
PHILLIPSBURG, N. J., June 28, 1906.

THE CLASSIFICATION OF COALS.[1]

BY S. W. PARR.

Received July 3, 1906.

THE fundamental properties of coal are directly involved in the decomposition products which are in evidence as a result of geological processes. These products have certain characteristics which manifest themselves in practical every-day use under the two notions of behavior and quality. A scheme of classification, therefore, to have any intelligent significance should be an expression of these two ideas. But while it should be susceptible of practical or commercial interpretation, it should have for its fundamental and ultimate basis, correct analytical facts and scientific data. The methods of classification thus far proposed have seemed to the writer deficient in one or the other of these two phases: either they were devised wholly with industrial ends in view and gave little heed to scientific considerations or they were too profoundly scientific to be capable of translation into any every-day meaning. The work here outlined has been done in connection with the State Geological Survey of Illinois and the effort has been made to embody both of these phases in the consideration of the topic.

The scheme of classification at present most widely recognized is that proposed by Frazer.[2] It has the merit of being intelligible from the industrial standpoint. It does not, however, embody certain phases that seem desirable if any meaning attaches to our discussion of the essentials from a scientific basis as above set forth. Indeed in his recent admirable defense of this classification,[3] Frazer recognizes the lack of data which at the present time would be embodied in the ordinary results of proximate analysis.

It is proposed by Campbell[4] to base a classification on the ratio of the total carbon divided by the total hydrogen. The argument

[1] Read at the Ithaca Meeting of the American Chemical Society.

[2] Trans. Am. Inst. Min. Eng. 6, 430.

[3] Bull. Am. Inst. Min. Eng. March, 1905.

[4] Report of Coal Testing Plant, U. S. Geol. Survey, St. Louis, Professional Paper U. S. G. S. No. 48, Part I, pp. 156–173.

for the use of the total hydrogen in such a ratio seems illogical and at variance with all the facts attending the property of coals. Especially is this true at the lignitic end of the series. Certain it is that the hydrogen there has a different meaning from what it has at the semi-bituminous end. To include the hydrogen of the moisture is to build on a variable that would make it impossible for any one else to reproduce the classification who could not duplicate the exact method of sampling and transmission. With the finely drawn distinctions in the resulting ratios a sample of coal might fall into as many different classes as there were analysts who examined it. It fails also to make use of one valuable fact developed by the usual method of proximate analysis, and that is, the relation of the volatile hydrocarbons to the total carbonaceous material. This, it would seem, comprises such fundamental properties, both with reference to its chemical structure as well as its performance in actual use, that no system of classification could have much value that ignores it. These objections all become accentuated when samples approach the lignitic type. It does not seem possible that these divisions can be properly considered without taking into account the factor for combined water, the "residual cellulose," if we may so designate it. On this point again we quote from Frazer:[1] "It may well be that other factors than carbon and hydrogen will some day furnish the means of a further differentiation of lignites, brown coals, peats and cannel coals."

It is certain that in any careful study of the composition, especially of bituminous coals and lignites, there is truly another factor which seems to have been entirely ignored or overlooked and it is this factor which seems to be primarily the one to be made use of for further differentiating between not only the various sorts of bituminous coals, but especially between the bituminous coals and lignites, as well as between the lignites themselves. Reference has already been made to this constituent, which is the "water of hydration" or that part of the volatile matter which is non-combustible or inert, so far as fuel value is concerned. There is no part of the ordinary proximate analysis that refers to it and its only recognition so far seems to be in that part of Dulong's formula which represents the available hydrogen as consisting

[1] Bull. Am. Inst. Min. Eng. March, 1906, pp. 244-245.

of $H - \frac{O}{8}$, which in reality means the total hydrogen less the hydrogen required to combine with the oxygen of the coal. But here again this particular factor is obscured for the reason that the usual ultimate analysis combines in its factors the ordinary moisture as well as this water of composition, and it seems to be not altogether an easy matter to establish a recognition of this constituent of coal as a part of the volatile matter which should receive separate mention and report.

Another difficulty in the case has been the almost universal use of the term "volatile combustible" for "volatile matter," when as a matter of fact, it is not strictly a volatile combustible for the reason that in average bituminous coal approximately one-third of the volatile matter is really non-combustible. This may be further illustrated by putting into molecular form the pure coal of an average bituminous sample, considered as free from moisture and ash, as follows:

				Volatile matter.		
$C_{22}H_{20}O_3$	=	C_{16}	+	C_6H_{14}	+	$_3H_2O$.
Coal.		Fixed carbon.		Volatile combustible.		Inert.
Per cent.		Per cent.		Per cent.		Per cent.
100		58		26		16

This type molecule represents an actual example of Illinois coal and the right-hand member of the equation represents the percentage constituents of the products resulting from destructive distillation. It is not, of course, intended that these formulas represent actual compounds.

Now the point here made is that the two last constituents which are ordinarily reported as "volatile combustible," or still worse as "volatile carbon," are in fact composed of volatile hydrocarbons and hydrogen which are combustible and an inert constituent consisting essentially of hydrogen and oxygen in the proportion to form water, and hence designated as the inert portion of the volatile matter.

Furthermore, if we examine a lignite in the same way, we shall find the proportion of inert volatile matter much greater than in the case of bituminous coals and similarly, the semi-bituminous type will be found to have relatively less of this constituent.

The method of classification herein proposed, therefore, makes prominent use of that part of the volatile matter which has been variously designated as inert or non-combustible, or as "water of composition."

But still another factor even more fundamental must be taken into the account. It has already been referred to as the fact of chief value developed by the process of proximate analysis; this is the ratio existing between the forms of carbon. The amount of fuel constituent which assumes the volatile condition is as much a scientific item as it is a matter of practical importance. This is best expressed in the form of a ratio or percentage and while it may be argued that one ratio is as good as another, a thorough examination of the one here employed will bear out the argument that it best expresses that feature of the composition of coal which recognizes a certain percentage of the fuel as of the volatile sort. The ratio thus employed is designated by the expression $vc \times \frac{100}{C}$ in which "vc" is the volatile carbon unassociated with hydrogen, and "C" is the total carbon as determined by analysis.

Briefly outlined, the plan of classification proposes to retain the old nomenclature but to base the first or fundamental divisions upon the ratio $vc \times \frac{100}{C}$. Upon applying this principle it will be found that coals in general divide themselves first into two distinct classes. Those of the anthracitic and those of the bituminous type. In the first division (of the one hundred coals tabulated), no carbon ratio as above expressed is found greater than 15 per cent. In the second division, no carbon ratio falls below 20 per cent. This certainly has the virtue of differentiating between these two types in a manner which demands respectful consideration for this suggested ratio. As to further classification, also, this ratio seems to be all that is needed to differentiate among the members of the first general division. Three main classes are thus indicated: First, anthracites proper with a ratio of $vc \times \frac{100}{C}$ of less than 4; second, semi-anthracites with ratios falling between 4 and 8; and third, semi-bituminous with ratios grouping very closely around 10 and 12, but in no case exceeding 15.

In the second general division, designated as the bituminous type, we have again three general classes. But here there enters into the account the factor for the inert portion of the volatile matter. Moreover, in order to make one coal comparable with

another, this constituent has been reduced to the pure coal or "ash and water free" basis and expressed in percentage.

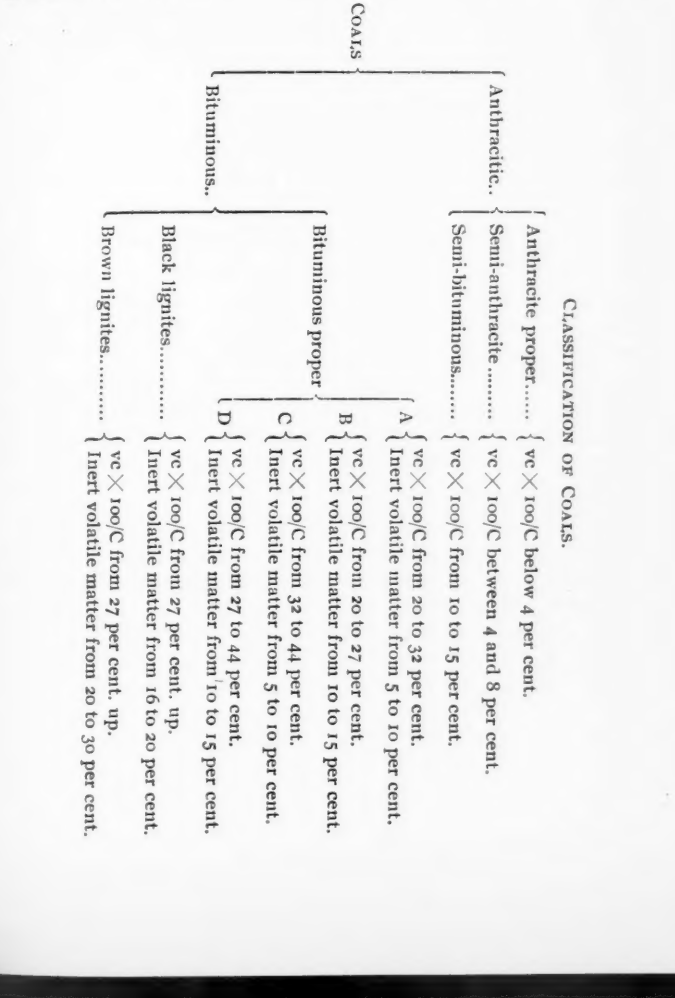
The three divisions, therefore, are designated as follows:

First, the bituminous proper with carbon ratios exceeding 20 and with inert volatile content not exceeding 15 per cent.

Second, black lignites with carbon ratios exceeding 27 and with inert volatile ratios falling between 16 and 20 per cent.

Third, brown lignites with carbon ratios above 27, but with inert volatile matter above 20 per cent.

The tabular presentation of this outline will make these relations more clear.


Classification of Coals.
Coals
Anthracitic..
Anthracite proper..... vc × 100/C below 4 per cent.
Semi-anthracite ..... vc × 100/C between 4 and 8 per cent.
Semi-bituminous..... vc × 100/C from 10 to 15 per cent.
Bituminous..
Bituminous proper
A vc × 100/C from 20 to 32 per cent. Inert volatile matter from 5 to 10 per cent.
B vc × 100/C from 20 to 27 per cent. Inert volatile matter from 10 to 15 per cent.
C vc × 100/C from 32 to 44 per cent. Inert volatile matter from 5 to 10 per cent.
D vc × 100/C from 27 to 44 per cent. Inert volatile matter from 10 to 15 per cent.
Black lignites..... vc × 100/C from 27 per cent. up. Inert volatile matter from 16 to 20 per cent.
Brown lignites..... vc × 100/C from 27 per cent. up. Inert volatile matter from 20 to 30 per cent.

One further subdivision is necessary: the bituminous group is large and is susceptible of further separation. These subclasses are designated for the present by the letters A, B, C, and D. A and B have the characteristic of a lower percentage of volatile carbon, using that term correctly, with a "fat" and a "lean" feature as indicated by the percentage of inert volatile matter, being from 5 to 10 per cent. under A, and from 10 to 15 per cent. under B. In exactly the same way C and D are characterized by having a high ratio of volatile carbon but sub-class C has the lower percentage of inert volatile matter, thus allying it closely with the cannels or gas coals, and D has the higher percentage of inert matter, thus bringing it nearer the lignites.

Before illustrating this method of classification by tabulating a series from analytical data, one point further should be discussed. That is the element of intrinsic value or relative merit. This enters slightly into the expression for the carbon ratios, but a coal with a high percentage of its fuel content in the fixed form may still be inferior in fuel content to one with a high ratio of volatile combustible.

So also something more of relative value is expressed by the percentage of inert volatile matter but this factor alone should not be made to carry the burden of indicating the grade. Concerning the element of worth it should not dominate in the idea of classification, and in the scheme here proposed this feature is considered as having been given its due weight by arranging particular coals in their ultimate classes in the order of their fuel ratios. Here again is proposed something of an innovation in the use of terms. If we recognize the true fuel of a coal to be all comprised in the total carbon, available hydrogen, and the sulphur, then the reciprocal of the sum of these percentages expressed in hundreds will be a fuel ratio that indicates directly the number of pounds of that particular coal required to make one hundred pounds of true combustible or "fuel," and to avoid confusion of terms, we designate this factor as the "gross coal index." For example, a West Virginia coal has carbon 78.31 per cent., hydrogen 4.31 per cent., and sulphur 0.90 per cent.; total fuel 83.5 per cent. Then the gross coal index $= \frac{100}{0.835}$ or 120, which means that 120 pounds of this coal would be required to make 100 pounds of actual fuel. Or again illustrating by a

sample of Dakota lignite: if we have carbon 52.66 per cent., hydrogen 1.83 per cent., and sulphur 2.02 per cent., total 56.51 per cent., the expression for the gross coal index would be $\frac{100}{0.565}$ or 175, which means that 175 pounds of this material would be required to make 100 pounds of true combustible matter.

In the following table, use is made of the analytical results as obtained at the United States Geological Survey Coal-Testing Plant at St. Louis. The ultimate order of the samples is arranged according to their fuel ratios as above described, while the location in the respective classes is determined by the carbon ratios and the inert volatile percentages as already outlined.

It may be said in conclusion that the analytical results from fifty coals by Lord and Haas previously made[1] and by Williams[2] have been subjected to the same method of classification with equally satisfactory results.

CLASSIFICATION OF COALS, ST. LOUIS TESTING PLANT, FIRST REPORT.

Anthracites.

$vc \times \frac{100}{C}$ below 4 per cent.

Semi-Anthracites.

$vc \times \frac{100}{C}$ between 4 and 8 per cent.

Arkansas No. 5	4.66
Arkansas No. 2	7.96

Semi-Bituminous.

$vc \times \frac{100}{C}$ from 10 to 15 per cent.

	Carbon ratio, $vc \times 100/C$.	Gross coal index.
West Virginia No. 10	11.63	110.0
West Virginia No. 6	13.26	113.0
West Virginia No. 7	10.68	113.5
West Virginia No. 11	10.55	120.0
West Virginia No. 5	11.06	120.0
Arkansas No. 3	11.41	123.0
Arkansas No. 1	10.00	124.5

[1] Trans. Am. Inst. Min. Eng. Vol. XXVII.

[2] Mich. Geol. Report, Vol. VIII.

UNIVERSITY OF ILLINOIS, URBANA, ILL.

BITUMINOUS.

CLASS A.

vc × 100/C 20 to 32 per cent.
Inert volatile matter 5 to 10 per cent.

	Carbon. Ratio.	Inert vol. matter.	Gross coal index.
West Va., No. 9 ...	21.02	8.46	118.5
West Va., No. 8 ...	25.18	7.78	119.0
West Va., No. 5 ...	21.46	6.33	120.0
West Va., No. 4 ...	20.89	8.03	120.0
West Va., No. 1 ...	29.30	9.53	120.0
Kansas, No. 5	23.54	8.75	120.5
West Va., No. 3 ...	23.30	8.22	123.0
Kansas, No. 3	25.80	7.51	127.0
Kansas, No. 4	28.02	7.97	129.5
Kansas, No. 1	26.69	8.27	131.5
Kentucky, No. 4...	29.63	9.73	134.0
Kansas, No. 2	24.56	7.88	136.5

BLACK LIGNITES.

vc × 100/C 27 per cent. and above.
Inert volatile matter 16 to 20 per cent.

N. Mexico, No. 1...	27.10	16.88	147.0
Montana, No. 1.....	28.77	18.25	153.5
Colorado, No. 1.....	29.60	19.19	155.0
Wyoming, No. 2...	32.36	17.00	160.5
Wyoming, No. 1...	32.27	19.99	161.0
N. Mexico, No. 2..	33.29	16.18	164 0

CLASS B.

vc × 100/C 20 to 27 per cent.
Inert volatile matter 10 to 15 per cent.

	Carbon. Ratio.	Inert vol. matter.	Gross coal index.
Kentucky, No. 1...	27.11	10.54	120.0
Alabama, No. 1.....	25.56	10.51	130.0
Alabama, No. 2.....	25.27	12.77	135.0
Illinois, No. 3	22.50	11.75	137.0
Iowa, No. 1	24.74	10.08	142.0
Illinois, No. 6	21.50	14.83	146.5
Iowa, No. 5	25.66	13.84	150.0

CLASS C.

vc × 100/C 32 to 44 per cent.
Inert volatile matter 5 to 10 per cent.

Missouri, No. 4.....	38.61	7.41	121.0
West Va., No. 2 ...	32.16	9.44	121.5
Missouri, No. 1.....	32.05	9.53	145.5

BROWN LIGNITES.

vc × 100/C 27 per cent. and above.
Inert volatile matter 20 to 30 per cent.

Texas, No. 2.....	30.00	23.90	165.0
N. Dakota, No. 2..	28.40	23.79	172.0
N. Dakota, No. 1 ..	36.17	21.09	175.0
Texas, No. 1.....	44.20	22.39	180.0

CLASS D.

vc × 100/C 27 to 44 per cent.
Inert volatile matter 10 to 15 per cent.

	Carbon. Ratio.	Inert vol. matter.	Gross coal index.
Indian Terr., No. 2...	30.35	11.53	130.0
Indian Terr., No. 3...	29.86	11.36	132.5
Indian Terr., No. 1...	28.34	11.86	132.5
Kentucky, No. 2.....	31.59	11.91	133.0
Kentucky, No. 3.....	29.64	11.76	135.0
Indiana, No. 2.....	32.09	11.44	140.5
Iowa, No. 3	35.68	11.23	141.0
Indian Terr., No. 4..	30.54	13.46	141.5
Illinois, No. 1.....	33.73	12.77	143.5
Illinois, No. 4	28.30	13.41	145.5
Iowa, No. 2.....	30.85	12.56	145.5
Indiana, No. 1.....	31.40	12.00	146.5
Iowa, No. 4	32.70	11.93	147.0
Illinois, No. 5	29.90	14.15	154.0
Missouri.....	30.63	12.12	155.0
Missouri, No. 3.....	28.61	13.05	162.0
Illinois, No. 2	32.96	12.95	163.0
Indian Terr., No. 5...	29.28	13.44	168.0

AN IMPROVED COLORIMETER.

By William Gabb Smeaton.

Received July 5, 1906.

The instrument permits an accurate comparison of the heights of two columns of liquid enclosed between parallel glass plates. Reflectors consisting of a ground glass plate superposed over a plate of opal glass, are adjusted to project parallel rays from the source of light (Welsbach) vertically through the solutions under investigation.

The solutions are contained in glass cylinders of approximately 33 mm. inside diameter and 100 mm. height, ground plane at the bottom and closed by a plate of the best mirror glass. Each cylinder carries a side arm and stand-pipe near the bottom. During a series of measurements the side arm is connected with a reservoir containing the solution in question, which permits the introduction of any quantity of solution into the cylinder. The latter is placed in a brass sheath to shut off horizontal light. Sheaths and cylinders are fitted in grooves on a metal plate which has circular openings 32 mm. in diameter for the transmission of the light and adjustment of a float cylinder.

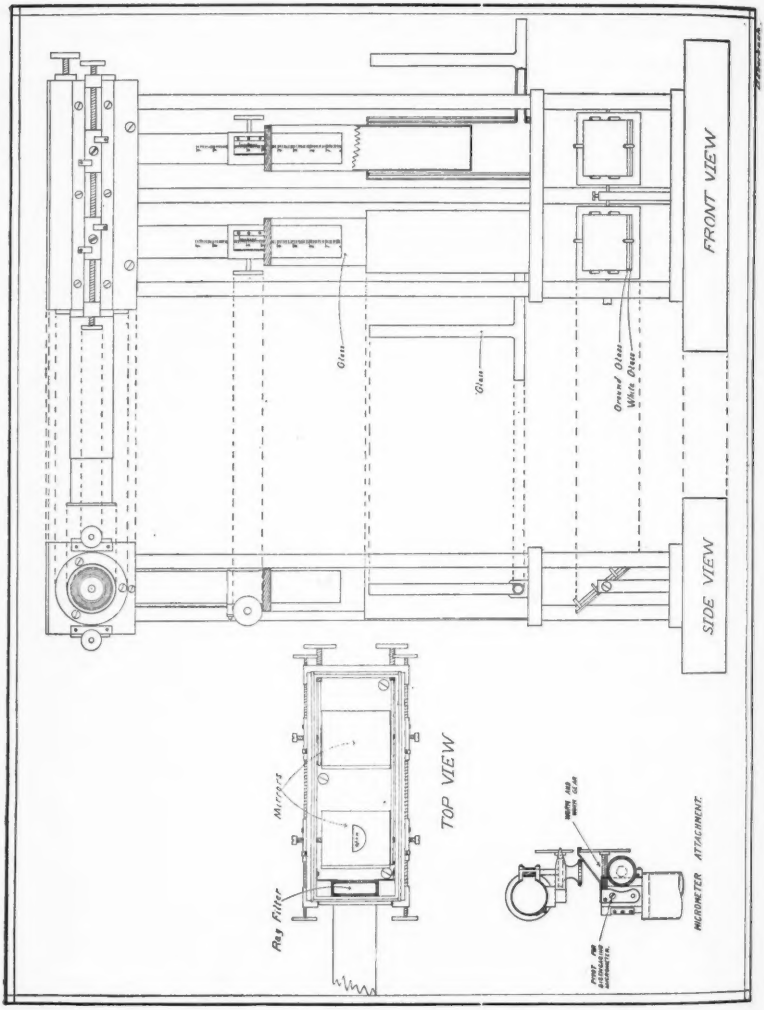
The height of the liquid column is adjusted by a glass float cylinder, 30 mm. in outside diameter, 110 mm. long, ground plane at the bottom and closed also by a plate of the best mirror glass. This cylinder is movable vertically over a brass tube by means of a rack and pinion. It is adjusted so that the two glass plates of the respective cylinders are exactly parallel.

The brass tubes are 22 mm. in external diameter and 125 mm. long. They are permanently attached to a metal plate and have a millimeter scale reading upwards. A vernier indicating 0.1 mm. is riveted to a short brass tube which carries the pinion. To the lower edge of this brass tube the glass float is cemented.

The upper part of the apparatus consists of a box riveted to the metal plate to which the brass tubes are attached. The inside measurements are: width, 45 mm.; height, 47 mm.; length, 130 mm. At one end projects a telescope tube with a total length of 175 mm. when drawn out. The orifice is a pinhole and diaphragms of suitable dimensions may be attached to the inner end of the draw-tube.

The light passing vertically through the solution impinges on

plane glass mirrors above the openings of the brass tubes and is deflected horizontally through the telescope tube. By means of a series of springs these mirrors can be adjusted in three planes. A portion of the silver coating of the mirror next to the telescope



tube is removed, thus giving passage to the beam from the rear mirror. The principle is therefore that of the Donnan colorimeter. The form and dimensions of the silver surface removed will be a matter of personal choice. I have tried many different forms and prefer to use the instrument as a half-shade apparatus, diaphragming the field to about 5 or 6 mm. diameter. When desirable a light filter is used to increase the delicacy of observation.

Measurements are made by comparing the solution in question with some standard. The millimeter scale and vernier are used when the height of the liquid column is several centimeters. To permit accurate comparisons with solutions only a few millimeters in height a simple micrometer, reading 0.01 mm., has been devised. This attachment is thrown into service by a pivot and can be released when not needed.

A high degree of accuracy can be attained if the eye has been trained to make color comparisons for several weeks. In working with various copper- and nickel-ammonia complexes I have repeatedly checked observations to 0.1 mm. The micrometer attachment has been devised only recently and consequently I am not yet in a position to state the ultimate delicacy of the observations recorded with this instrument.

The apparatus has a compact form, as is evident from the diagram. It is, moreover, inexpensive. As a substitute for the etched scale on the brass tube a paper scale such as is provided with galvanometers might be used. It is necessary, of course, to calibrate both the millimeter scale and the micrometer. For very accurate measurements a zero reading is made with each determination by lowering the float cylinder until the two glass plates are in contact, the scale having such a range that this zero reading is always positive.

ANN ARBOR, June 18, 1906.

ANTIMONY IN BABBITT AND TYPE METALS.

BY H. YOCKEY.

Received July 23, 1906.

IN the May number of this Journal a paper by the author of this article appeared describing the analysis of Babbitt metal as practiced in this laboratory. Antimony was described as being determined by the method of Walters and Apfelder. Since appearing, a number of objections to this method have been received

by me and from such well-known chemists that I could not ignore them, so I determined to try to better the method if I could. The following method is the result of these experiments. By this method antimony can be determined accurately in alloys containing tin and antimony; lead and antimony; lead, tin and antimony; tin, copper and antimony; lead, tin, copper and antimony; and lead, copper and antimony. In these alloys the copper never exceeded 7 per cent. What would be the results with a high copper content, I have not determined.

Treat 1 gram filings with 1 gram potassium iodide, 40 cc. water and 40 cc. concentrated hydrochloric acid (sp. gr. 1.2), and boil gently one hour. Filter on asbestos in a Gooch crucible, washing five or six times with hot dilute hydrochloric acid (1 : 10).

Wash the precipitate and asbestos into a 150 cc. beaker with a little wash-water, and add 20 or 25 cc. concentrated hydrochloric acid and a few crystals of potassium chlorate. Cover with a watch-glass and warm gently, stirring occasionally.

When the antimony is in solution dilute to 100 cc. and filter the asbestos out, washing until the wash-water shows no hydrochloric acid. Boil vigorously five minutes to free the solution from free chlorine. Cool to room temperature, add 1 gram of potassium iodide in solution and titrate the liberated iodine with a standard thiosulphate solution.

The following results were obtained by this method. The alloys were all made from new commercially pure metals by myself.

	Taken Per cent.	Found. Per cent.	Per cent.
1. Pb	54.	....	....
Sn	22.	....	....
Sb	22.	21.95	22.08
Cu	2.	....	....
2. Pb	45.42	....	....
Sn	40.14	....	....
Sb	14.44	14.57	14.46
Cu	....	....	....
3. Pb	76.	....	....
Sb	24.	24.12	23.91
4. Pb	43.	....	....
Sn	50.	....	....
Sb	6.5	6.45	6.45
Cu	0.5	....	....
5. Pb	84.	....	....
Sb	15.	15.03	15.12
Cu	1.	....	....

The last example I give is the result on an alloy sent me by the Pittsburg Section of the American Chemical Society for analysis. The alloy contained, as reported to me after I had sent in my report, the following: 4.98 to 5.02 per cent. copper, 14.70 per cent. antimony, and the balance tin. My report by this method was 14.73 per cent. antimony, the average of two determinations.

NATIONAL LEAD CO.,
CINCINNATI BRANCH.

THE ETCHING TEST FOR SMALL AMOUNTS OF FLUORIDES.

BY A. G. WOODMAN AND H. P. TALBOT.

Received July 31, 1906.

IN THE course of some work on the detection of fluorides in malt liquors it was found necessary to make a study of the etching test on glass as commonly employed, both from its standpoint as a qualitative test and with a view to making it approximately quantitative.

As a qualitative test, the etching method was found eminently satisfactory, as regards delicacy and reliability, if carried out under proper conditions. The procedure employed was the same in principle as that proposed by Blarez,[1] later modified by Leach,[2] and adopted as a provisional method by the Association of Official Agricultural Chemists.[3] It may be described briefly as follows: To 150 cc. of the liquid to be tested add 10 cc. of potassium sulphate (33 grams per liter), heat the solution to boiling and while boiling add slowly from a burette or pipette 10 cc. of a 10 per cent. barium acetate solution. Continue the boiling for a moment and then set the beaker aside for the precipitated barium sulphate and fluoride to settle. In most cases, unless the precipitate settles very readily, it is preferable to let it stand over night. The clear supernatant liquid is decanted, the precipitate transferred to a filter, washed and ignited in a platinum crucible. An alternative method which is more rapid and has the added advantage of avoiding the use of filters, is to decant off the clear liquid and wash the precipitate into one of the tubes of a centrifugal machine. The sedimented material is then washed directly into a platinum

[1] Chem. News, 91, 39 (1905).
[2] Ann. Rept. Mass. State Board Health, 1905.
[3] U. S. Dept. Agr., Bur. Chem., Circular 28.

crucible. This is placed in the centrifugal machine and whirled again, after which the precipitate can be ignited over a flame.

Meanwhile a small glass plate, clear and free from scratches, is thoroughly cleaned and coated on one side with a mixture of equal parts paraffin and carnauba wax. This can readily be done by pouring a little of the melted wax on the warmed plate. If the excess is drained off and the glass held level, a thin uniform wax coating will result. While the coating is still warm make a characteristic mark, such as a small cross (+), in the wax with a pointed instrument, taking care that the glass is laid bare but not scratched. The precaution should be taken to have the cross of approximately the same size in the different tests; for example, with arms about 4 mm. long and 1 mm. wide. On the uncoated side of the plate locate the cross by marks placed at the ends of the arms with a diamond or file.

To the precipitate in the crucible add 2 to 3 cc. of concentrated sulphuric acid, hold the crucible in the tongs, and heat its upper edge cautiously and quickly in a small flame. Press the glass plate quickly down on the warm crucible, having the cross nearly in the center, and hold it a moment to seal the glass securely to the crucible. The crucible should be embedded in the wax so firmly that it can be lifted by the plate. Support the crucible in a piece of heavy asbestos board in which a hole has been cut so that the crucible fits closely, put two or three drops of water on the glass plate and press down on it a condenser, the lower end of which is closed by a piece of thin sheet rubber such as is employed by dentists. Heat the crucible for an hour by a small flame about 9 mm. long placed 6 mm. below the bottom of the crucible. At the end of this time remove the plate, scrape off the wax and clean the glass on both sides, with "bon-ami" or other polishing material which will not scratch the glass. Examine it by reflected light for an etching. A test should not be considered positive unless the cross can be seen when viewed from either side of the glass.

Several times during the hour it may be necessary to put a drop of water on the plate around the edge of the condenser, to keep the wax from melting.

It is hardly necessary to speak of the need for using the purest reagents obtainable and testing them carefully by blank tests. The barium acetate has given the most trouble from traces of fluorides and it has been found best to prepare it from recrystallized

barium nitrate by precipitating with ammonium carbonate, dissolving the washed carbonate in acetic acid, and recrystallizing the barium acetate.

The condenser may be made from a piece of wide glass tubing arranged so that a constant current of cold water may be kept flowing through it and with a piece of thin sheet rubber (dental dam), stretched tightly over the bottom. The diameter of the tube should be somewhat greater than that of the platinum crucible. A "carbon funnel," as shown in the figure, has been found to answer well.

The electric stove, as recommended by Leach, has not given good results in our hands for furnishing a uniform source of heat, it being our experience that different stoves, and even different sides of the same stove, vary considerably in temperature. On account of the larger surface radiating heat it is more difficult to prevent the melting of the wax than when the small flame is used.

The delicacy of the procedure above described, as tested on aqueous solutions of potassium fluoride, is rather surprising. A perfectly distinct etching is readily obtained from 150 cc. of solution containing 1 : 10,000,000 of fluorine, and by careful working it is possible to get a recognizable test from 1 : 50,000,000. By a recognizable test is meant one which is visible from either side of the glass and does not have to be brought out by breathing on the glass. Care should be taken to clean the glass with "bon-ami" before examining it, since sulphuric acid alone will give a "stain" which can be brought out by breathing on it, and might easily be mistaken for an etching. The scouring will always remove this, however.

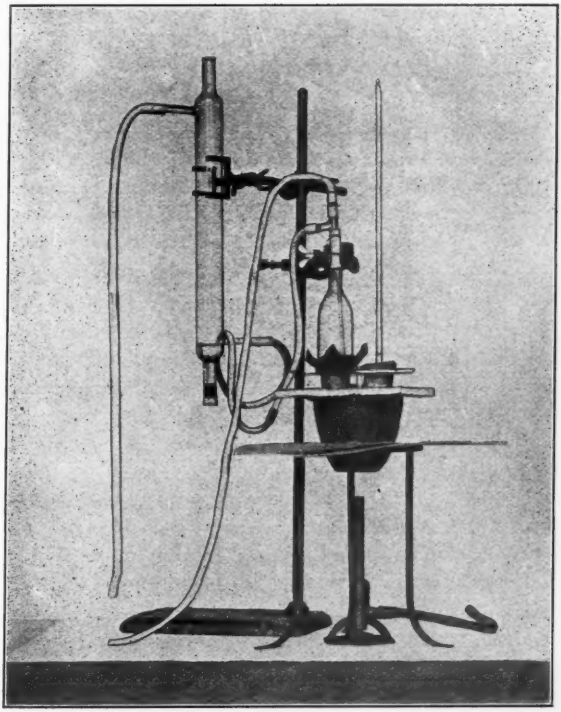
It has been found best to continue the heating for at least an hour. The etching obtained with a small amount of fluorine, say 1 : 5,000,000, is distinctly less after fifteen or thirty minutes than if the heating is continued for the longer period. There seems to be, however, no advantage in prolonging the test above an hour.

It is best to have the area of glass exposed approximately the same in different tests, because the intensity of the etching produced evidently depends somewhat upon the area of glass exposed. Tests made with 1 : 100,000 of fluorine showed that a test in one case indicating apparently 25 or 30 times as much fluorine as in another could be obtained by simply exposing that much more glass. The presence of organic matter or of traces of

water during the etching does not seem to make much difference except in the character of the mark obtained. In the absence of organic matter, and when the contents of the crucible are perfectly dry, the resulting etching is usually a "matt" etching, resembling ground glass. If moisture is present, either originally or resulting from the action of organic matter on the sulphuric acid, the etching is clear and transparent and somewhat more difficult to detect.

It was noticed early in the investigation that the test would not infrequently fail to give a positive result even when fluorides were known to be present. This led to a somewhat detailed study of the conditions during the precipitation and the etching in order to see if in any part of the procedure a lack of strict adherence to minor detail was the reason why a successful test could not be obtained. Without giving a minute description of the numerous experiments, it may be said that considerable variations in the manner of carrying out the precipitation made no apparent difference in the result. The precipitate settles better and slightly more uniform results are obtained when the precipitation is made slowly and at the boiling temperature, although good results have been obtained repeatedly by adding the reagents in the cold and then heating to boiling. The experiments showed, however, that one factor is extremely important—essential in fact,—namely, the temperature during the etching. This one factor was found sufficient to explain the failures experienced, a difference of 15° or 20° in temperature being enough to prevent the obtaining of a test with a given amount of fluoride.

The differing results obtained at varying temperatures led to an attempt to base an approximately quantitative method on the temperature factor, since something more than a qualitative test is necessary to distinguish between natural and added fluorides. Traces of fluorine are widely distributed in food products and the mere fact that an etching can be obtained is not evidence that fluorides have been added as a preservative. It is essential to know approximately the proportion of fluoride present and the temperature-effect seemed to offer a simple means of determining this. The usual methods for determining fluorine in minerals are, of course, not applicable to the minute quantities that have to be considered here. The objection of lack of delicacy applies also to the various methods based on the loss in weight sustained by



glass of known composition when subjected to the action of hydrofluoric acid. A comparison of the etchings obtained in different tests as regards their apparent intensity has not proven satisfactory in our experience and the same has been found true by others.[1] In order to render such comparisons reliable the etchings must be made by the use of special apparatus to maintain exact conditions, whereas in a test of this kind, if it is to be available for use in general analytical practice, simplicity of apparatus is an important consideration.

With this idea in view, a series of experiments have been carried out on known fluoride solutions in order to determine the temperature corresponding to a definite amount of fluorine. In all cases the fluorine has been precipitated from 150 cc. of solution by means of barium acetate and potassium sulphate, as described above. In fact, up to the point of making the etching test, the procedure is exactly the same as in making a qualitative test.

The apparatus used for heating the crucible during the etching was a simple form of air-bath consisting of a large nickel or iron crucible provided with an asbestos cover in which two platinum crucibles are inserted at equal distances from the center. These two crucibles should be similar in size and shape. One crucible, as shown in the figure, is provided with a waxed plate and condenser, the other with an asbestos lid through which projects a thermometer reaching to the bottom. This control crucible contains 2–3 cc. of concentrated sulphuric acid. The heat is furnished by a burner centrally placed beneath the large crucible. After the apparatus is once adjusted and in working order it should be kept intact and undisturbed. The platinum crucibles should always occupy the same positions and it is necessary to determine, by means of two thermometers whose relative values are known, what temperature on the control thermometer corresponds to the desired temperature in the "etching crucible." This should be done for each of the "etching temperatures" stated below.

It will be realized that an apparatus so simple has its limitations, and in the work which has been done it has not been attempted to control the temperature closer than 5° on either side of the desired point.

As the result of numerous tests, the following temperatures

[1] Ost: Ber. 26, 152.

have been fixed, the corresponding amounts of fluorine being stated in each case.

Temperature.	Distinguishes between.
79°–82°	1 : 25,000 and 1 : 100,000.
113°	1 : 100,000 and 1 : 1,000,000.
136°	1 : 1,000,000 and 1 : 5,000,000.
173°–178°	1 : 5,000,000 and 1 : 25,000,000.
213°–218°	1 : 25,000,000 or less.

This statement means that by running the test for an hour at 136° (131–141°), for example, a distinct etching will be obtained with one part of fluorine in 1,000,000; no test whatever will be given by a dilution of 1 : 5,000,000. Each of these temperature points has been fixed as the result of numerous tests with the apparatus described and they are believed to be definite. It is probable that by more closely regulating the temperature during the etching, the results could be made more nearly quantitative, but it was felt undesirable to attempt this at present on account of the necessary complication of apparatus.

In making a test on a solution containing an unknown amount of fluorine the precipitation is made in the usual manner and the etching carried on for an hour at the lowest temperature (79–82°), counting from the time when the corresponding temperature is reached in the control crucible. At the end of the hour the plate is removed, the crucible taken in the tongs, its upper edge gently warmed, and a fresh plate applied. If upon examining the plate just removed no etching is apparent, the test is continued for an hour at the next higher "etching temperature," and so on until a test is obtained or the absence of fluorides is shown. This has been done with a number of unknown solutions with very satisfactory results.

If it can be shown as a result of the examination of pure samples that the fluorine present naturally in a given food material is not above a certain maximum amount, then for the purpose of indicating the presence of added fluorides the test could be materially shortened, it being necessary to make the test at only one temperature. It is hoped to continue the investigation along this line in the future and to examine numerous samples of food and raw products with a view to determining the limiting values for their fluorine content.

In conclusion, it gives us much pleasure to record our indebted-

ness to Mrs. L. C. Krueger, to whom the credit for the analytical work is largely due.

MASS. INSTITUTE OF TECHNOLOGY,
BOSTON, MASS.

DETERMINATION OF URANIUM AND VANADIUM.

BY A. N. FINN.

Received July 30, 1906.

A STUDY of the ore carnotite, which is a potassium uranyl vanadate, repeatedly required the determination of uranium and vanadium. This led to a comparison of the various titration methods that have been suggested.

Bělohoubek[1] refers to the reduction of uranium in solution by zinc and sulphuric acid and titration with potassium permanganate. Sutton, in the sixth edition of his "Volumetric Analysis," states that this method is very accurate if care is taken to insure complete reduction which requires from one-quarter to one-half an hour.

Determinations of uranium by this method in solutions of uranyl sulphate gave very satisfactory results provided the potassium permanganate solution was not more than twentieth-normal. When, however, uranium is to be determined from a complex mixture or an ore, great difficulty is found in securing the uranium in a form sufficiently pure for the titration. This is especially true in the presence of vanadium.

The general method of separating the uranium and vanadium from each other and from the various other elements in the ore, is to treat an acid solution of the ore with an excess of sodium carbonate, which precipitates the iron, aluminum, etc., and filter. The filtrate containing the uranium and vanadium is acidified, the carbon dioxide expelled by boiling and the solution is made alkaline with sodium, potassium or ammonium hydroxide. This precipitates the uranium as the corresponding uranate, while the vanadium remains in solution. The uranate is dissolved in sulphuric acid, reduced with zinc and titrated with permanganate. The solution of vanadium is acidified, reduced with sulphur dioxide and titrated with permanganate.

The precipitated uranate is gelatinous and it was found impossible to wash this precipitate free from vanadium, and since

[1] J. pr. Chem. 99, 231.

the uranate is slightly soluble it is not desirable to wash or redissolve it many times.

In view of this fact, it became necessary to find an accurate and, if possible, a quicker method for the separation and determination of uranium and vanadium.

This was accomplished by precipitating the uranium in alkaline solution as a phosphate. This precipitate, ammonium uranyl phosphate, is not gelatinous, is insoluble and may easily be washed free from vanadium.

To show that the volumetric method of titrating the reduced solutions with permanganate is consistent in itself, samples of uranium salts containing no vanadium were used and the following results were obtained:

Sample.	Grams.	Per cent. U_3O_8.
Solution No. I	9.5058	3.195
	5.1820	3.120
	5.0603	3.167
	5.1570	3.135
Solution No. II	10.2941	5.084
	10.2839	5.056
Solution No. III	11.7228	5.228
	4.4641	5.276

Samples of solution No. III precipitated with ammonia, ignited and weighed as U_3O_8, gave the following results:

Grams.	Per cent. U_3O_8.
3.81955	5.237
5.3409	5.297

For vanadium, material free from uranium was used and the following results were obtained:

Sample.	Grams.	Per cent. V_2O_5.
Solution No. IV	10.7412	0.945
	10.4142	0.946
	11.3310	0.941
	11.4935	0.947
Solution No. V	12.8359	1.338
	12.6929	1.340
	15.2051	1.349
	14.1954	1.339
Sample No. VI	0.3311	39.127
	0.4341	39.170
	0.3004	39.200

The method suggested for determining uranium and vanadium is, in detail, as follows:

Dissolve a sample of ore that does not contain more than 0.25 gram of U_3O_8 in sulphuric acid (1:5) and evaporate to fumes of the acid. Cool, dilute, add an excess of sodium carbonate and boil until the precipitate settles well. Filter and wash with hot water. Dissolve the precipitate in the smallest possible amount of sulphuric acid, dilute, add an excess of sodium carbonate, boil, filter and wash. Acidify the combined filtrates and wash-waters with sulphuric acid. Add ammonium phosphate (0.5 gram is usually sufficient), heat to boiling and make alkaline with ammonia, boil for a few minutes, filter and wash with hot water containing a little ammonium sulphate, which prevents the finely divided particles of the precipitate from passing through the paper.

The filtrates now contains the vanadium and the precipitate the uranium. Acidify the filtrate with sulphuric acid, pass sulphur dioxide into it until it becomes blue, boil to expel the excess of sulphur dioxide and titrate while hot with permanganate. The iron factor of the permanganate solution multiplied by 1.631 gives the V_2O_5 factor or by 0.9159 gives the vanadium factor.

Dissolve the ammonium uranyl phosphate in sulphuric acid, add some granulated zinc and let the action continue vigorously for at least thirty minutes. Remove the undissolved zinc by filtering over asbestos, using a suction pump, and titrate at about 60° with permanganate (twentieth-normal).

The iron factor of the permanganate solution multiplied by 2.5167 gives the U_3O_8 factor or by 2.133 gives the uranium factor.

By this method of separation, reducing the solutions and titrating with permanganate, the following results were obtained:

Sample.	Grams.	Per cent. U_3O_8.	Per cent. V_2O_5.
Solution No. VII.....	10.7904	1.074	1.429
	21.5602	1.068	....
	15.0921	1.085	1.407
	10.6119	1.063	1.415
Ore-carnotite I.....	1.0002	11.793	6.363
	1.0013	.....	6.300
	1.0004	11.885	6.261

Sample.	Grams.	Per cent. U_3O_8.	Per cent. V_2O_5.
Ore-carnotite II.....	1.0009	6.755	6.849
	2.0005	6.702	6.526
Ore-carnotite III	1.0006	4.873	5.128
	1.0003	4.945	5.358
Ore-carnotite IV	1.00045	1.834	....
	1.00025	1.728	....
Ore carnotite V.....	0.9994	0.4094	....
	1.2004	0.4205	....

CHEMICAL LABORATORY,
UNIVERSITY OF DENVER.

THE SOLUBILITY OF SILVER CHLORIDE IN HYDROCHLORIC ACID AND IN SODIUM CHLORIDE SOLUTIONS.

BY WILLIAM EDWARD BARLOW.

Received August 17, 1906.

IT HAS been shown by Dudley[1] that when sodium dioxide is fused in a silver crucible the metal is rapidly attacked, with the formation of a complex oxide.

In 1902 I observed, in ignorance of Dudley's paper, the same action, and showed[2] that when the melt is evaporated or heated with hydrochloric acid (as in the method of determining sulphur by means of fusion with sodium dioxide) the altered silver is converted into chloride, which dissolves (in amounts varying with the temperature and concentration) in the concentrated salt solution present. If the solution is then filtered, and allowed to stand, the greater part—but not the whole—of the silver chloride deposits on cooling. The barium sulphate precipitates from such determinations are almost certain to contain silver. When the solution is filtered hot, and barium chloride solution added before cooling, as in the ordinary sodium peroxide process for determining sulphur, the amount of silver in the barium sulphate may be considerable. In one case 0.03 gram silver chloride was extracted from such a precipitate. This would have occasioned an error of 0.2 per cent. in the sulphur content.

To ascertain the extent to which the reactions above mentioned go on under the conditions of a sodium peroxide fusion the following experiments were made:

[1] Am. Ch. J. 28, 62 (1902).

[2] Inaugural Dissertation, Göttingen, June, 1903.

(*a*) 22.5 grams of sodium chloride, an amount corresponding to the 15 grams of sodium peroxide used in a fusion, were dissolved in 200 cc. of boiling water, and silver nitrate solution was added to the hot solution until a permanent precipitate was produced. The liquid was then quickly filtered clear, and the dissolved silver was precipitated with hydrogen sulphide. The weight of silver sulphide found corresponded to 0.03 gram silver chloride.

(*b*) The above experiment was repeated, using, however, 400 cc. of water. The silver chloride dissolved was 0.027 gram. Two or three drops of the silver nitrate solution gave a permanent precipitate in the cold solution. A little of this cold solution, filtered perfectly clear, gave a brown coloration with hydrogen sulphide, showing that small amounts of silver chloride dissolve in such solutions even in the cold.

(*c*) Twenty-three grams of sodium chloride in 400 cc. of cold water, with about 8 cc. of concentrated hydrochloric acid, dissolved 0.01 gram silver chloride in the cold.

Attempts were then made to estimate volumetrically the amounts of silver chloride taken up by various solutions of sodium chloride and hydrochloric acid. Silver nitrate solution (of known silver content) was added from a burette to the solution to be tested, until, with moderate stirring, a faint white cloud of silver chloride remained. The burette was read, the salt solution brought to 50°, and the addition of silver nitrate continued until a permanent precipitate was again produced. The titration was then made at about 90° in the same solution.

The results of these titrations are tabulated below. In every case the same amount of sodium chloride was used, 23 grams, corresponding to the 15 grams of sodium peroxide used in a fusion. When acid was used it was present in the proportion of 10 cc. of the concentrated acid to 290 cc. of solution. The solutions marked with asterisks were of approximately the same concentration as the filtrate from a peroxide fusion as regards sodium chloride, although they contained somewhat larger amounts of acid.

The results from 100 cc. in Series A and C are probably rendered low by the dilution of the solution with the 15 or 16 cc. of silver nitrate solution. In all other cases the dilution is small enough to have a negligible effect under the conditions described.

The silver nitrate solution contained 0.01485 gram of the salt

per cubic centimeter, corresponding to 0.012525 gram silver chloride per cubic centimeter.

Volume of solution. cc.	20°. cc. of $AgNO_3$ solution needed.	50°. cc. of $AgNO_3$ solution needed.	About 90°. cc. of $AgNO_3$ solution needed.	Corresponding weight of AgCl.
Series A.—23 grams of sodium chloride alone.				
100	2.50	7.10	15.70	0.1966
150	1.15	2.30	9.80	0.1227
200	0.50	2.00	7.60	0.0952
300*	0.30	1.40	5.95	0.0745
400*	0.15	1.10	4.55	0.0569
500*	0.10	1.00	4.20	0.0526
700	0.10	0.90	3.90	0.0488
Series B.—10 cc. of conc. HCl in each 300 cc. solution.				
100	0.05	0.12	0.35	0.0043
150	...	0.18	0.70	0.0086
200	0.10	0.25	0.90	0.0112
300*	...	0.35	1.35	0.0169
400*	0.20	0.50	1.90	0.0238
500*	...	0.60	2.20	0.0275
700	0.20	0.75	3.20	0.0400
Series C.—Sodium chloride and HCl together.				
100	2.20	5.70	16.00	0.2004
150	1.50	3.80	10.50	0.1315
200	0.80	2.90	9.30	0.1165
300*	0.40	2.10	7.50	0.0939
400*	0.35	1.50	6.70	0.0839
500*	0.35	1.80	6.80	0.0852
700	0.45	2.00	7.70	0.0964

In the following table the sums of the results of Series A and B, at 90°, are placed side by side with the corresponding results of C.

Volume of solution. cc.	Sums of results of A and B. cc.	Results of Series C. cc.
100	16.05	16.00
150	10.50	10.50
200	8.50	9.30
300	7.30	7.50
400	6.45	6.70
500	6.40	6.80
700	7.10	7.70

The figures show that the solubility of silver chloride in solutions of sodium chloride falls off (at a gradually diminishing rate) with diminishing concentration, and that the amounts of silver chloride dissolved in the acid are directly proportional to the volumes of acid (of fixed concentration) used. The increase in

solubility near the end of Series C is due to the larger amounts of acid present. The results of C correspond nearly enough with the sums of A and B to show that the effects of the sodium chloride and acid are independent. These facts become even more evident when the results are expressed in the form of curves.

It is clear that the use of a silver dish for sulphur determinations by fusion with sodium dioxide introduces complications. The removal of the dissolved silver is best effected by precipitation with perfectly pure hydrogen sulphide. Dilution to 400 cc., and filtering after cooling, does not suffice to remove all the silver. Dilution to a much larger volume would involve either a tedious evaporation over the alcohol lamp before precipitation with barium chloride or a considerable error, owing to the solubility of barium sulphate in the large volume of solution. It is simpler and more satisfactory to avoid the difficulty by using a nickel crucible or dish.

METALLURGICAL LABORATORY,
VIRGINIA POLYTECHNIC INSTITUTE.

[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 124.]

RESEARCHES ON QUINAZOLINES (SIXTEENTH PAPER). SYNTHESIS OF 6-NITRO-2-METHYL-4-KETODIHYDROQUINAZOLINES FROM 5-NITROACETANTHRANIL AND PRIMARY AMINES.[1]

BY MARSTON TAYLOR BOGERT AND ELLEN PARMELEE COOK.

Received July 13, 1906.

IN previous papers[2] we have reported upon 5- and 7-nitro-4-ketodihydroquinazolines. The following article contains a record of some experiments in the synthesis of derivatives of the 6-nitro isomer.

Dehoff,[3] by the direct nitration of 2-methyl-4-ketodihydroquinazoline, obtained a nitro derivative in which the position of the nitro group remained unknown until Thieme[4] prepared the same substance by heating the ethyl ester of 5-nitro-2-acetamino-

[1] Read at the meeting of the New York Section of the American Chemical Society, May 11, 1906.

[2] Bogert and Chambers: This Journal, 27, 649 (1905); Bogert and Seil: Ibid. 27, 1305 (1905); 28, 884 (1906); Bogert and Steiner: Ibid. 27, 1327 (1905).

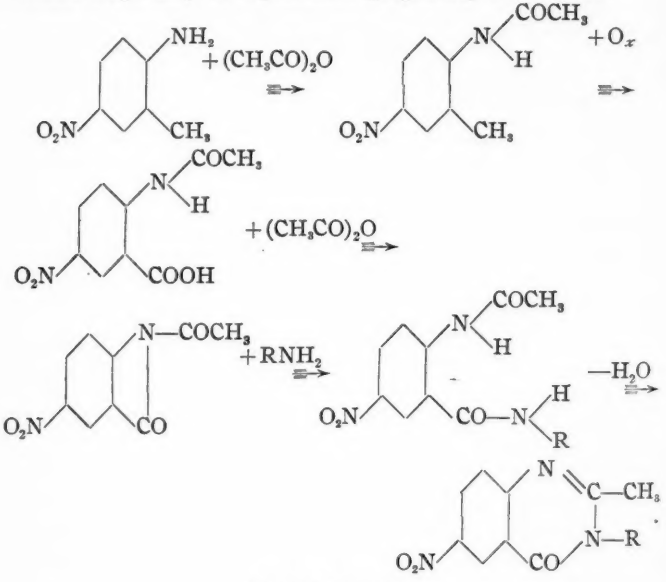
[3] J. pr. Chem. [2] 42, 347 (1890).

[4] Ibid. [2] 43, 473 (1891).

benzoic acid with alcoholic ammonia at 170°, thus fixing the position of the nitro group at 6 in the quinazoline nucleus. Both Dehoff and Thieme prepared also the 2,3-dimethyl-6-nitro-4-ketodihydroquinazoline, and in 1896 Kratz[1] obtained the 3-amino-6-nitro-4-ketodihydroquinazoline.

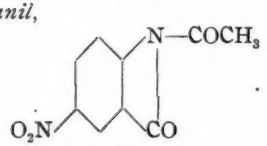
We have prepared a few derivatives of 6-nitro-2-methyl-4-ketodihydroquinazoline by very simple methods, entirely similar to those used in the case of the 5- and 7-nitro isomers. 5-Nitro-2-toluidine was acetylated, the acetyl derivative oxidized to 5-nitro-acetanthranilic acid, the latter changed to 5-nitroacetanthranil, which yielded the nitroquinazolines when condensed with primary amines of various kinds.

These steps may be represented graphically as follows:



EXPERIMENTAL.

5-Nitroacetanthranil,



[1] J. pr. Chem. [2] 53, 224 (1896).

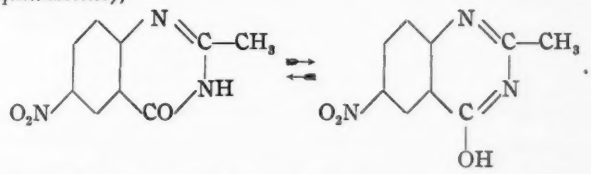
5-Nitro-2-toluidine was acetylated in the usual way, and the acetyl derivative crystallized from alcohol, when it showed a melting-point of 198°. This acetyl derivative was then oxidized by potassium permanganate in presence of magnesium sulphate. The 5-nitroacetanthranilic acid thus obtained melted after several recrystallizations at 221.5° (corr.). This agrees with the melting-point (221°) given by Ullmann,[1] but not with that reported by Seidel (213°).[2] The yield was about 65 per cent.

The nitroacetanthranilic acid was heated for five minutes with acetic anhydride, and the solution then allowed to cool. Long, colorless needles crystallized out, melting at 161–162° (corr.). The excess of acetic anhydride was removed by washing with dry ether or with carbon tetrachloride.

Calculated for $C_9H_8O_4N_2$: C, 52.42; H, 2.91. Found: C, 52.24 and 52.14; H, 2.92 and 2.76.

Like the other nitroacetanthranils, this hydrolyzes slowly in moist air, or rapidly when boiled with water, yielding the nitroacetanthranilic acid again.

6-Nitro-2-Methyl-4-Ketodihydroquinazoline (*6-Nitro-2-Methyl-4-Oxyquinazoline*),



5-Nitroacetanthranil was heated with dilute aqueous ammonia, the mixture then warmed with dilute potassium hydroxide solution to change any intermediate amide to quinazoline, and a current of carbon dioxide passed through the solution. The quinazoline precipitated as an amorphous powder, which was crystallized from hot alcohol.

The same product was obtained by dissolving the nitroacetanthranilic acid in an excess of dilute ammonium hydroxide solution, evaporating to dryness, and heating the residue at 125° in an oil-bath. The yield by this method was very poor.

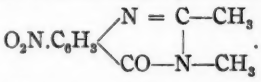
As already stated, this body was first prepared by Dehoff, and later by Thieme. The properties of the substance prepared by

[1] Ber. 36, 1801 (1903).

[2] Chem. Centr. 1902, II, 554.

us agree entirely with those of the compound obtained by Dehoff and Thieme, both in solubilities and melting-point. They both found that their product darkened between 230° and 280°, while ours begins to darken at about 266°, and melts at 278–281° (corr.).

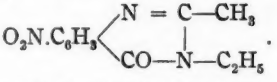
6-Nitro-2,3-Dimethyl-4-Ketodihydroquinazoline,



5-Nitroacetanthranil was warmed for a few minutes with methylamine, and the product recrystallized from alcohol. It then melted at 164–165° (corr.), and was insoluble in alkalies.

Dehoff[1] prepared this substance by heating the potassium salt of the 2-methyl compound with methyl iodide at 120°, and also by the action of fuming nitric acid (sp. gr. 1.5) upon 2,3-dimethyl-4-ketodihydroquinazoline, while Thieme made it from the corresponding silver salt and methyl iodide, and also by heating nitroacetanthranilic acid ethyl ester with methylamine for several hours at 130°. Both authors give the melting-point as 165°.

6-Nitro-2-Methyl-3-Ethyl-4-Ketodihydroquinazoline,

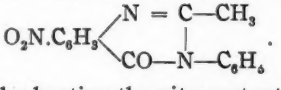


This was prepared in similar fashion from 5-nitroacetanthranil and ethylamine. It crystallizes from alcohol in needles which melt at 166° (corr.).

Calculated for $C_{11}H_{11}O_3N_3$: N, 18.02. Found: N, 18.07 and 17.95.

The same compound was obtained when the sodium salt of the nitromethylquinazoline was treated with ethyl iodide.

6-Nitro-2-Methyl-3-Phenyl-4-Ketodihydroquinazoline,

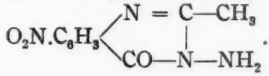


This was made by heating the nitroacetanthranil with aniline. It is difficultly soluble in alcohol, and crystallizes from glacial acetic acid in small, compact, light-yellow crystals, which melt at 219–220° (corr.).

Calculated for $C_{15}H_{11}O_3N_3$: N, 14.95. Found: N, 14.80.

[1] Loc. cit.

6-Nitro-2-Methyl-3-Amino-4-Ketodihydroquinazoline,



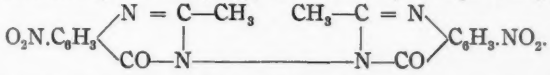
When the nitroacetanthranil was heated with a 50 per cent. aqueous solution of hydrazine hydrate, there resulted a deep-red solid, soluble in hot water. Colorless needles crystallized from the aqueous solution on cooling, which melted at 208–209° (corr.).

Calculated for $C_9H_8O_3N_4$: C, 49.09; H, 3.64; N, 25.45. Found: C, 49.00; H, 3.81; N, 25.56.

The compound is readily soluble in dilute alcohol, from which it crystallizes in long, colorless needles. It dissolves in solutions of the caustic alkalies with a deep red color.

When it was crystallized from glacial acetic acid and the crystals allowed to dry in the air, the compound showed a nitrogen content of 23.31 per cent. When this air-dried material was heated at 135° until the weight became constant, it lost 9.27 per cent. of acetic acid. This would make the nitrogen percentage in the substance dried at 135°, 25.68 per cent. On analysis, it was found to be 25.65 per cent. This appears to indicate the presence of acetic acid of crystallization in the proportion of two molecules of the acid to five of the quinazoline. This may not, however, represent the actual proportion between acid and quinazoline in the crystals as they first separate, as it is not unlikely that the crystals analyzed had already lost some of their acetic acid on standing in the air.

6,6′-Dinitro-2,2′-Dimethyl-4,4′-Diketotetrahydrodiquinazolyl,



One molecule of hydrazine (using a 50 per cent. aqueous solution of the hydrate) was added to two of the nitroacetanthranil, and the mixture heated for twenty minutes at 160–180° in an oil-bath. The cooled melt was pulverized and heated with alcohol, to remove aminoquinazoline, unchanged anthranil, and other impurities. The residual diquinazolyl was crystallized from glacial acetic acid. Small, compact crystals resulted, which melted with darkening at 281–286° (corr.). The yield was very poor.

Calculated for $C_{18}H_{12}O_6N_6$: N, 20.59. Found: N, 17.71 and 18.00.

These analytical results made it quite clear that we did not have the free diquinazolyl in hand. The air-dried substance was, therefore, dried to constant weight at 145°. In this drying at 145° it lost 12.1 per cent. of acetic acid, which would make the nitrogen percentage in the acetic acid-free substance, 20.3. The crystals analyzed apparently contained one molecule of the diquinazolyl to one of acetic acid.

Calculated for $C_{18}H_{12}O_6N_8.CH_3COOH$: N, 17.95.

HAVEMEYER LABORATORIES, COLUMBIA UNIVERSITY,
July, 1906.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES.

(SIXTH PAPER.)

BY TREAT B. JOHNSON.

Received July 19, 1906.

THE object of the work[1] described in this paper was to prepare some new thiol acids, I, and examine their behavior towards thiocyanates, II, and isothiocyanates, III.

R.COSH,	R.SCN,	R.NCS.
I.	II.	III.

It has been shown in several papers from this laboratory[2] that thiocyanates and isothiocyanates can be sharply distinguished by their behavior towards thiol acids, I. Thiocyanates, II, react with thiol acids in two ways. The most commonly observed reaction is a direct addition to the acid to give a dithiourethane, IV. Certain ones, on the other hand, react in a complicated manner to give thiol esters, V, and thiocyanic acid, VI.

$$\underset{\text{I.}}{\text{R.COSH}} + \underset{\text{II.}}{\text{R}'\text{.SCN}} = \underset{\text{IV.}}{\text{R.CONHCSSR}'}.$$

$$\underset{\text{I.}}{\text{R.COSH}} + \underset{\text{II.}}{\text{R}'\text{.SCN}} = \underset{\text{VI.}}{\text{HSCN}} + \underset{\text{V.}}{\text{R.COSR}'}.$$

Alkyl isothiocyanates, VII, and acyl isothiocyanates, VIII, react

[1] All the experimental work described in this paper was accomplished by advanced Senior students (1906), who had completed the required laboratory course in practical organic chemistry.—T. B. JOHNSON.

[2] Wheeler and Merriam: This Journal, **23**, 283; **24**, 439; Wheeler and Johnson: Ibid. **24**, 680; **26**, 185; Wheeler and Jamieson: Ibid. **24**, 744.

in an entirely different manner with thiol acids to form substituted acid amides. IX, and carbon bisulphide as follows:

$$\underset{\text{VII.}}{R'.NCS} + R.COSH = \underset{\text{IX.}}{R.CONHR'} + CS_2.$$

$$\underset{\text{VIII.}}{R'CO.NCS} + R.COSH = \underset{\text{IX.}}{RCONHCOR'} + CS_2.$$

The above reactions have hitherto been applied with only two thiol acids, *viz.*, thiolbenzoic, X, and thioacetic acids, XI. It seemed of interest to the writer to decide whether other thiol

$$\underset{\text{X.}}{C_6H_5COSH} \quad \text{and} \quad \underset{\text{XI.}}{CH_3COSH}$$

acids might be used to distinguish between thiocyanates and isothiocyanates. Furthermore, we wished to determine whether the tendency for a thiocyanate to give a dithiourethane, IV, or a thiol ester, V, might be influenced by the negative character of the thiol acid.

We describe in this paper four new thiol acids, *viz.*, phenylthioacetic, $C_6H_5CH_2COSH$, meta- and parabromthiobenzoic, $Br.C_6H_4COSH$, and metanitrothiobenzoic, $NO_2C_6H_4COSH$, acids. They were prepared by dissolving the corresponding acid chlorides in an aqueous or alcoholic solution of potassium hydrosulphide and then treating the resulting potassium salts with hydrochloric or sulphuric acids.

$$R.COCl + 2KSH = R.COSK + KCl + H_2S$$
$$R.COSK + HCl = R.COSH + KCl.$$

Meta- and parabromthiobenzoic acids and metanitrothiobenzoic acid are of especial interest as the first members of this class of thiol acids that have been obtained as solids at ordinary temperature. They were very stable and could be kept for several weeks without change in a dry atmosphere. Phenylthioacetic acid was obtained as an oil.

Carius[1] has described a solid thiosalicylic acid, $OH.C_6H_4COSH$. He prepared it by acting on salicylic acid with phosphorus pentachloride and then treating the acid chloride with barium hydrosulphide. It does not seem probable that Carius was dealing with this thiol acid, since Anschütz and his co-workers[2] have shown that phosphorus halides do not react with salicylic acid to give the acid chloride, $HO.C_6H_4COCl$. The first oxy-acid chloride

[1] Ann. **129**, 11.

[2] Ibid. **228**, 308; **239**, 316, 333; **239**, 304.

isolated was 3,5-dichlorsalicyl chloride, $Cl_2(HO).C_6H_2COCl$.[1] Anschütz and his students have recently described a large number of aromatic oxy-acid chlorides.[2]

We examined the behavior of the above thiol acids towards methyl, ethyl and benzyl thiocyanate. They reacted with these thiocyanates to give the corresponding dithiourethanes. The reactions were very smooth and we did not detect any evidence of the formation of thiol esters. So far as we were able to judge, the four acids did not show any appreciable difference in their tendency to combine with thiocyanates.

Our thiol acids reacted normally with an isothiocyanate. Phenylthioacetic, parabromthiobenzoic and metanitrothiobenzoic acids reacted quantitatively with phenyl isothiocyanate to give the corresponding acid anilides.

Phenylacetanilide, $C_6H_5CH_2CONHC_6H_5$.[3]

Parabrombenzoylanilide, $\overset{4}{Br}.C_6H_4\overset{1}{C}ONHC_6H_5$.[4]

Metanitrobenzoylanilide, $\overset{3}{NO_2}.C_6H_4\overset{1}{C}ONHC_6H_5$.[5]

COMPARATIVE BOILING- AND MELTING-POINTS OF THE THIOL ACIDS USED IN OUR THIOCYANATE RESEARCHES, AND THE BOILING- AND MELTING-POINTS OF THEIR CORRESPONDING ACID CHLORIDES.

Acid Chloride	B. P.	M. P.
Acetyl chloride, CH_3COCl	55°	..
Phenylacetyl chloride, $C_6H_5CH_2COCl$	102° at 17 mm.	..
Benzoyl chloride, C_6H_5COCl	198°	..
Metabrombenzoyl chloride, $\overset{3}{Br}.C_6H_4\overset{1}{C}OCl$	243°	..
Parabrombenzoyl chloride, $\overset{4}{Br}.C_6H_4\overset{1}{C}OCl$	..	41°
Metanitrobenzoyl chloride, $\overset{3}{NO_2}.C_6H_4\overset{1}{C}OCl$	..	35°
Thiol Acid.		
Thioacetic acid, CH_3COSH	93°	..
Phenylthioacetic acid, $C_6H_5CH_2COSH$	..	..
Thiobenzoic acid, C_6H_5COSH	..	24°
Metabromthiobenzoic acid, $\overset{3}{Br}.C_6H_4\overset{1}{C}OSH$	..	58°
Parabromthiobenzoic acid, $\overset{4}{Br}.C_6H_4\overset{1}{C}OSH$	..	78–79°
Metanitrothiobenzoic acid, $\overset{3}{NO_2}.C_6H_4\overset{1}{C}OSH$	..	89–90°

[1] Anschütz: Ann. 346, 300; Ber. 30, 221.

[2] Ann. 346, 286–360.

[3] Hofmann: Ber. 13, 1225.

[4] Raveill: Ann. 222, 178.

[5] Schotten: Ber. 21, 2245.

EXPERIMENTAL PART.

By Ernest Bateman, Erik Schjöth Palmer and Charles Andrew Brautlecht.

Phenylthioacetic Acid, $C_6H_5CH_2COSH$.—This acid was obtained in the form of its potassium salt when phenylacetyl chloride was warmed on the steam-bath with an aqueous solution of potassium hydrosulphide. After the acid chloride had completely dissolved the solution was acidified with sulphuric acid. The thiol acid separated as a limpid oil. It did not solidify after standing for several weeks. When exposed to the atmosphere it was slowly oxidized to the disulphide.

Diphenylacetyl Disulphide $(C_6H_5CH_2COS)_2$.—This compound was prepared by suspending finely pulverized iodine in an aqueous solution of the sodium salt of phenylthioacetic acid. The sulphide separated as a crystalline deposit. It was purified for analysis by recrystallization from 95 per cent. alcohol. It deposited in transparent plates that melted at 62°. It was insoluble in sodium hydroxide solution. Carbon and hydrogen determinations gave: C, 63.73; H, 5.0; calculated for $C_{16}H_{14}O_2S_2$, C, 63.57; H, 4.63.

Action of Phenylthioacetic Acid on Phenyl Isothiocyanate.—Molecular proportions of phenylthioacetic acid and phenyl isothiocyanate were heated together at 100°. Carbon bisulphide was evolved and we obtained a crystalline substance. It deposited from 95 per cent. alcohol in prisms that melted at 117–118°. It was identified as phenylacetanilide.[1] It did not contain sulphur and when mixed with phenylacetanilide the melting-point was not lowered.

Phenylacetyldithiomethylcarbamate, $C_6H_5CH_2CO.NH.CSSCH_3$.—Molecular proportions of phenylthioacetic acid and methyl thiocyanate were heated together in a boiling water-bath for about one hour. We obtained a thick oil that solidified on cooling. The compound crystallized from alcohol in slender prisms that melted at 133° to an oil. They were dissolved by sodium hydroxide and were reprecipitated from the alkaline solution by acids. The analysis (Kjeldahl) gave: N, 6.24; calculated for $C_{10}H_{11}ONS_2$, 6.22.

Phenylacetyldithioethylcarbamate, $C_6H_5CH_2CO.NH.CSSC_2H_5$.—This compound was obtained when a mixture of molecular proportions of phenylthioacetic acid and ethyl thiocyanate was heated

[1] Hoffman : Loc. cit.

at 100° for three hours. It deposited from alcohol in lemon-yellow prisms that melted at 125° to an oil. The analysis (Kjeldahl) gave, N, 5.74; calculated for $C_{11}H_{13}ONS_2$, 5.85.

Phenylacetyldithiobenzylcarbamate, $C_6H_5CH_2CO.NH.CSSCH_2C_6H_5$. —From phenylthioacetic acid and benzyl thiocyanate. It was purified for analysis by recrystallization from alcohol. It deposited in lemon-yellow prisms that melted at 123°. The analysis gave: N, 4.68; calculated for $C_{16}H_{15}ONS_2$, 4.65.

Metabromthiobenzoic Acid, $\overset{3}{Br}.C_6H_4.\overset{1}{C}OSH$.—Metabrombenzoyl chloride[1] did not react readily with potassium hydrosulphide in aqueous solution. In order to obtain a complete reaction it was necessary to heat them at 100° for several hours. When the alkaline solution was acidified with hydrochloric acid the thiol acid separated as an oil. This oil was extracted with ether and the solution dried over calcium chloride. When the ether was removed by distillation we obtained the thiol acid as an oil which finally solidified. It was crystallized from petroleum ether and deposited as a light yellow, crystalline powder that melted at 58°. The acid was very soluble in alcohol, ether and benzene. The analysis gave: Br, 36.35. Calculated for C_7H_5OBrS, 36.85.

Metabrombenzoyldithiomethylcarbamate, $\overset{3}{Br}.C_6H_4.\overset{1}{C}ONHCSSCH_3$. —This compound was prepared by heating a mixture of metabromthiobenzoic acid and methyl thiocyanate in a boiling water-bath for a few minutes. It deposited from 95 per cent. alcohol in distorted needles that melted at 124°. The analysis gave: N, 5.1; calculated for $C_9H_8ONBrS_2$, 4.83.

Metabrombenzoyldithioethylcarbamate, $\overset{3}{Br}C_6H_4.\overset{1}{C}O.NHCSSC_2H_5$. —From metabromthiobenzoic acid and ethyl thiocyanate. It deposited from alcohol in needle-like prisms that melted at 131°. The analysis gave: N, 4.3; calculated for $C_{10}H_{10}ONBrS_2$, 4.60.

Metabrombenzoyldithiobenzylcarbamate, $\overset{3}{Br}.C_6H_4\overset{1}{C}ONHCSSCH_2C_6H_5$.—From benzyl thiocyanate and metabromthiobenzoic acid. It deposited from 95 per cent. alcohol in prismatic crystals. They melted at 113°. The analysis gave· N, 4.0; calculated for $C_{15}H_{12}ONBrS_2$, 3.82.

Parabromthiobenzoic Acid,[2] $\overset{4}{Br}.C_6H_4.\overset{1}{C}OSH$.—When parabrom-

[1] Sudborough: J. Chem. Soc. **67**, 590.

[2] This acid was first prepared by Dr. G. S. Jamieson in 1903.

benzoyl chloride was added to an alcoholic solution of potassium hydrosulphide an immediate reaction took place with separation of potassium chloride. The solution was warmed a few minutes to complete the reaction, then concentrated to a small volume and the insoluble potassium chloride removed by filtration. When the filtrate was cooled we obtained a deposit of yellow prisms. They were very soluble in water and were identified as the potassium salt of parabromthiobenzoic acid. A bromine determination gave: Br, 30.85; calculated for C_7H_4OBrSK, 31.35.

When this potassium salt was dissolved in cold water and the solution acidified with hydrochloric acid the thiol acid deposited in the form of colorless, flat prisms. It dissolved in hot alcohol and deposited on cooling in prisms that melted at 78–79° to a clear oil. A bromine determination gave: Br, 36.50; calculated for C_7H_5OBrS, 36.85.

Action of Parabromthiobenzoic Acid on Phenyl Isothiocyanate.—When the thiol acid was heated with the isothiocyanate an immediate reaction took place with evolution of carbon bisulphide. We obtained a compound that deposited from alcohol in plates. They melted at 201–202° to a clear oil and did not respond to a test for sulphur. A nitrogen determination (Kjeldahl) agreed with the calculated value in *parabrombenzoylanilide*,[1] $\overset{4}{Br}C_6H_4\overset{1}{C}ONHC_6H_5$. Found, 5.3; calculated for $C_{13}H_{10}ONBr$, 5.07.

This same anilide[2] melting at 201–202° was also prepared by warming the thiol acid with a molecular proportion of aniline.

Parabrombenzoyldithiomethylcarbamate, $\overset{4}{Br}.C_6H_4\overset{1}{C}O.NHCSSCH_3$.—From parabromthiobenzoic acid and methyl thiocyanate. It deposited from 95 per cent. alcohol in distorted needles that melted at 152° to a clear oil. The analysis gave: N, 4.80; calculated for $C_9H_8ONBrS_2$, 4.82.

Parabrombenzoyldithioethylcarbamate, $\overset{4}{Br}.C_6H_4.\overset{1}{C}O.NH.CSSC_2H_5$.—From ethyl thiocyanate and parabromthiobenzoic acid. It deposited from alcohol in pale yellow needles that melted at 116° to a yellow oil. The analysis gave: N, 4.63; calculated for $C_{10}H_{10}ONBrS_2$, 4.60.

Metanitrothiobenzoic Acid, $\overset{3}{NO_2}.C_6H_4\overset{1}{C}OSH$.—This acid was ob-

[1] Loc. cit.

[2] Raveill states that this anilide melts at 197°. Ann. 222, 178.

tained in the form of its potassium salt by adding metanitrobenzoyl chloride to an aqueous or alcoholic solution of potassium hydrosulphide. When an aqueous solution of the salt was acidified with sulphuric or hydrochloric acid the thiol acid separated as an oil which soon solidified. This acid is unstable if moist, and all operations must be performed at low temperatures in order to avoid decomposition. The acid was insoluble in water, but very soluble in acetone, warm alcohol and benzene. It deposited from dilute alcohol in light yellow, prismatic crystals that showed signs of melting at 85° and then melted sharply at 89–90° to a clear oil. The analysis gave: N, 7.69 and 7.7; calculated for $C_7H_5O_3NS$, 7.65.

The sodium salt was very soluble in water. It deposited from 95 per cent. alcohol in irregular prisms. The analysis gave: N, 6.85; calculated for $C_7H_4O_3NSNa$, 6.82.

Action of Metanitrothiobenzoic Acid on Phenyl Isothiocyanate.—A mixture of molecular proportions of the isothiocyanate and thiol acid was heated in a boiling water-bath for about two hours. Carbon bisulphide was copiously evolved. We obtained a crystalline substance that was difficultly soluble in water. It deposited from alcohol in plates that melted at 154° and did not respond to a test for sulphur. A nitrogen determination agreed with the calculated value in *metanitrobenzoylanilide*,[1] $\overset{3}{NO_2}.C_6H_4\overset{1}{C}ONHC_6H_5$. The analysis gave: N, 12.0; calculated for $C_{13}H_{10}O_3N_2$, 11.6.

Metanitrobenzoyldithiomethylcarbamate, $\overset{3}{NO_2} . C_6H_4 . \overset{1}{C}O . NH CSSCH_3$.—This compound was prepared by heating together molecular proportions of methyl thiocyanate and metanitrothiobenzoic acid. The reaction was very smooth and complete in a few minutes. The urethane was very soluble in benzene and sparingly soluble in alcohol. It deposited from benzene in yellow needles that melted at 162°. The analysis gave: N, 10.64; calculated for $C_9H_8O_3N_2S_2$, 10.93.

Metanitrobenzoyldithioethylcarbamate, $\overset{3}{NO_2}.C_6H_4.\overset{1}{C}O.NH.CSSC_2H_5$. —From ethyl thiocyanate and metanitrothiobenzoic acid. This compound was sparingly soluble in cold alcohol and deposited from hot alcohol in yellow prisms that melted at 158° to a

[1] Schotten : Ber. 21, 2245.

clear oil. The analysis gave: N, 10.5; calculated for $C_{10}H_{10}O_3N_2S_2$, 10.37.

NEW HAVEN CONN.,
July 16, 1906.

THE CHLOR-HYDROCHLORIDES OF PINENE AND FIRPENE.

BY G. B. FRANKFORTER AND FRANCIS C. FRARY.

Received August 2, 1906.

The Purification of Pinene and Firpene.—The pinene used in the preparation of the following compounds was obtained from the common white turpentine by distilling with steam, drying and redistilling until the boiling-point was constant at 156–157°. An analysis showed that the substance consisted entirely of hydrogen and carbon, and the physical properties corresponded with those of pure pinene.

The firpene used was obtained from the western fir by distilling the crude pitch with steam. The water-white terpene was dried and redistilled several times. Combustion gave numbers which corresponded with the formula $C_{10}H_{16}$. Molecular weight determinations also gave numbers which corresponded well with the above formula. Its odor, its specific gravity, its refractive index and its optical activity differed from the pure pinene. The chemical properties, likewise, differed from pinene. The following is a comparison of the physical properties of the two substances:

	Pinene.	Firpene.
Boiling-point	156°–157°	153°–153.5°
Sp. gr. at 20°	0.8647	0.8598
Index of refraction at 20°	1.46336	1.47299
Optical activity $(\alpha)_D$	+14.34	−47.2

Preparation of Pinene Hydrochloride.—The pinene hydrochloride prepared by the common method contains a considerable quantity of soluble oily and resinous matter from which it is separated with great difficulty. In fact, we were unable to find a satisfactory method for the separation of the hydrochloride from these oily and resinous substances. A new method therefore seemed important. After many trials, the following process was finally chosen as being entirely satisfactory. Pure pinene was mixed with about an equal volume of dry chloroform in a large round-bottomed flask, mixed thoroughly and cooled below 0°. Pure

dry hydrochloric acid gas was passed into the liquid until it became saturated with the acid.

It was necessary to pass the gas into the pinene very slowly at first as considerable heat is generated. After saturation, an equal volume of water was added and the excess of acid removed by the addition of sodium bicarbonate. This mixture was immediately subjected to steam distillation. The chloroform which passed over first contained a considerable quantity of the hydrochloride; the greater part, however, remained in the flask after all the chloroform had been removed. Further steam distillation carried it over into the condenser where it solidified in comparatively pure form. The chloride still contained a very small quantity of a colorless oil. All the resinous matter, however, was completely removed. After most of the hydrochloride had distilled over, the oil began to appear. It is important that the solid chloride should be removed from the condenser before the oil begins to pass over as they readily mix and are difficult to separate from each other. It was found that the hydrochloride could be removed by cooling to —30°, filtering off the crystals and drying between sheets of filter-paper. Two or three crystallizations of the chloride from alcohol gave a substance which melted at 130–131°, which is the melting-point of pure pinene hydrochloride as stated by Long.[1] This method has been used in the preparation of all of the hydrochlorides and hydrobromides of both pinene and firpene and of the terpene from the Norway pine.

CHLOR-HYDROCHLORIDES OF PINENE AND FIRPENE.

Pinene Pentachlorhydrochloride, $C_{10}H_{11}Cl_5HCl$.—Several chlorine compounds have been prepared from pinene, the most important of which are nitrosyl-chloride[2] pinene dichlorhydrochloride[3] of questionable composition and trichloride of dipentene.[4] These and a few other compounds have been described but owing to the difficulty experienced in purifying them, only the above-mentioned compounds have been studied. Most of these chlorides were made by difficult complex methods which have been tried by others and found to give a mixture of several compounds with such closely associated properties that separation seems to us

[1] This Journal, 21, 637.
[2] Ibid. 9, 554 (1887).
[3] J. Russ. Chem. Soc. 25, 383.
[4] Ann. 270, 196.

next to impossible. Hypochlorous acid has been mentioned in a number of experiments. This reagent gives impure oxychlorterpenes which could not be separated. In a single other case, Hesse[1] used chlorine in a carbon disulphide solution. Examination of this method showed that in each case the reaction was deep-seated and several compounds, often of oily nature, were formed, together with sulphur and sulphur compounds.

Many different methods were tried by others without satisfactory results. Hydrochloric acid with potassium permanganate was finally tried and found to give good results. The method adopted was as follows: A known weight of the terpene hydrochloride was dissolved in 5 times its weight of pure chloroform and an equal quantity of water added and stirred. An equal weight of potassium permanganate was added and hydrochloric acid (sp. gr. 1.2) added cautiously. The flask was corked and allowed to stand for some time. Fresh additions of hydrochloric acid and permanganate were added from time to time. The process was continued for a week, taking care to keep an excess of chlorine in the solution. The chloroform was then separated from the water and a few drops of alcohol added to absorb the excess of chlorine. The chloroform solution was of a yellowish green color, due to the presence of free chlorine. After removing the chloroform by evaporation, the solid amorphous residue was crystallized from warm alcohol, dissolved in ether, clarified with bone-black and recrystallized several times from alcohol.

The crystallized substance resembled somewhat the original pinene hydrochloride in belonging to the isometric crystal system. The corrected melting-point, however, was 173–174°.

These crystals were deliquescent in both ether and chloroform vapors. Evaporation of the ether and chloroform left an amorphous substance. The presence of alcohol, however, reproduced the crystals. Analyses of the pure substance gave the following numbers:

0.2250 gram substance gave 0.5619 gram AgCl.

0.2044 gram substance gave 0.2586 gram CO_2 and 0.0562 gram H_2O.

Calculated for $C_{10}H_{12}Cl_6$: C, 34.74; H, 3.51; Cl, 61.69. Found: I. Cl, 61.75; II. C, 34.50; H, 3.05.

[1] Ann. 270, 196.

An attempt to make the pentachloride directly from pinene instead of the hydrochloride by chlorinating with hydrochloric acid and potassium permanganate, failed. The result in every attempt was a heavy oily mass with distinctly aromatic odor. This oil readily decomposed in the air, changing to a brown mass.

From the fact that this compound can not be prepared without first converting the terpene into the hydrochloride, we have represented it as well as the other analogous chlorine compounds which follow as a hydrochloride.

Pinene Hexachlorhydrochloride, $C_{10}H_{10}Cl_6HCl$.—Pinene hydrochloride was dissolved in chloroform and treated with dry chlorine in bright sunlight. Chlorine was passed into the solution for eight hours. Upon evaporation a residue was left which resembled somewhat the pentachloride. It was purified by recrystallizing from alcohol several times or until the melting-point became constant at 218°. The chlorine determination gave results higher than the theoretical but near enough to indicate that the compound is a hepta compound, 66.51 per cent. of chlorine being found. Calculated for $C_{10}H_{10}Cl_6HCl$, 65.43 per cent.

Pinene Nonachlorhydrochloride, $C_{10}H_8Cl_9HCl$.—In the preparation of pinene hexachlorhydrochloride, there was left in solution after the hexachlor compound had crystallized out of carbon tetrachloride, a sticky substance which refused to crystallize. This substance was dissolved in pure carbon tetrachloride and dry chlorine passed through the solution until it remained a bright yellow color after standing six hours in bright sunlight without the further addition of chlorine. Upon evaporation of the tetrachloride a waxy sticky mass remained, having about the consistency of "grained honey." No further reaction seemed to take place after standing several months. This waxy mass was then extracted with boiling 95 per cent. alcohol, when the oily part dissolved, leaving most of the crystals. By repeated extraction with large quantities of alcohol, the whole mass of crystals dissolved. Upon cooling the alcoholic solution, most of the substance crystallized out again. After recrystallization the substance had a melting-point of 263–264° (uncor.). Further recrystallization failed to change the melting-point.

Analysis of this substance gave the following results:

1. 0.1950 gram substance gave 0.5655 gram AgCl.
2. 0.1910 gram substance gave 0.5579 gram AgCl.
3. 0.1581 gram substance gave 0.3473 gram AgCl.
4. 0.1457 gram substance gave 0.3228 gram AgCl.

Calculated for $C_{10}H_7Cl_9HCl$: Cl, 73.47. Found: Cl, 71.69, 72.22, 72.14, 72.76.

It will be seen that the chlorine found is lower than the theoretical. It was at first thought that perhaps the substance was a mixture of nona- and decachlorhydrochloride. The constant melting-point, however, indicated a single substance. Finally, a molecular weight determination was made and the results obtained corresponded closely with the above theory.

The substance resembles the pentachlorhydrochloride in its crystal form and properties but it is much less soluble in alcohol and has less odor. Alcoholic silver nitrate did not remove any of the chlorine, while several months' standing with excess of silver oxide removed only a very small part of the chlorine. Sodium methylate in absolute alcohol seemed to have no effect upon it. Neither boiling nitric acid (sp. gr. 1.4) nor a boiling mixture of this with two parts sulphuric acid had any apparent effect upon it. It is more soluble in absolute alcohol than in 95 per cent. alcohol and is very soluble in benzene, ether, chloroform and carbon tetrachloride.

The Action of Bromine on the Hydrochloride.—It was found that bromine would not act readily upon the hydrochloride. The hydrochloride was exposed to the sunlight in the presence of bromine for a month, no change evidently having taken place during that time. By long treatment with hydrobromic acid in the presence of potassium permanganate and sulphuric acid, an aromatic oil was obtained. This oil proved to be a bromide but has not been obtained in pure enough state for analysis.

COMPOUNDS OF FIRPENE.

Firpene Hydrochloride, $C_{10}H_{16}HCl$.—Firpene hydrochloride was made by the same method given for the preparation of pinene hydrochloride. After crystallizing several times from alcohol the substance had a melting-point of 130–131°, the same as pinene hydrochloride, but differing from the latter by being more volatile and more soluble in nearly all the common solvents and having a slightly different odor. From chloroform and carbon tetra-

chloride, it is amorphous. Chlorine determinations gave the following:

1. 0.2760 gram substance gave 0.22723 gram of AgCl.
2. 0.2704 gram substance gave 0.22143 gram of AgCl.

Calculated for $C_{10}H_{16}HCl$: Cl, 20.55. Found: Cl, 20.39 and 20.25.

Firpene Dichlorhydrochloride, $C_{10}H_{14}Cl_2HCl$.—Firpene hydrochloride differs widely from pinene hydrochloride in its chemical properties, especially when treated with chlorine. Pinene hydrochloride will not form a dichlorhydrochloride but forms with excess of chlorine the hexachlorhydrochloride. Firpene hydrochloride on the contrary readily forms a dichlorhydrochloride, but repeated attempts to make higher chlorides were unsuccessful, the dichloride being always formed. The dichloride proved to be less volatile and less soluble in alcohol than the hydrochloride and more soluble than the pinene pentachloride.

Analysis gave 44.21 per cent. Cl; calculated for $C_{10}H_{16}Cl_2HCl$, 44.04.

Firpene Hydrobromide, $C_{10}H_{16}HBr$.—Firpene forms a well crystallized hydrobromide which differs entirely from the pinene hydrobromide. The method of preparation was the same as that used in the preparation of the hydrochloride. Thoroughly dried hydrobromic acid gas was passed into a chloroform solution of firpene. The crystalline substance was purified by recrystallizing from alcohol. The pure substance had a melting-point of 102°. The hydrobromide of pinene melts at 90°. The crystals seem to have a feathery form, are readily pressed into a gummy mass and are very volatile. It has a pronounced odor of camphor. It is soluble in nearly all the common organic solvents.

Bromine determinations gave 36.98 per cent. Br; calculated for $C_{10}H_{16}HBr$, 36.86 per cent.

Behavior of Pinene and Firpene with Nitrosyl Chloride.—One of the most characteristic and easily prepared compounds of pinene is the nitrosylchloride. The method given by Wallach[1] was followed to the letter with both pinene and firpene. The former gave without difficulty a fine crystalline substance while the latter gave no crystalline compound even after repeated trials. A small quantity of an oily substance obtained from firpene may have possibly been a nitrosochlor compound. In fact, this reaction seems to be a characteristic of firpene as well as of pinene.

[1] Ann. 253, 251; 245, 251.

The chlorine compounds made thus far are oils, no matter how much or how little chlorine has entered the compound. These oils are difficult to purify inasmuch as all of them decompose before the boiling-point is reached. We have had several compounds in hand but have as yet been unable to purify them. On the contrary both firpene and pinene when first converted into the hydrochlorides, form crystalline compounds of chlorine, the melting-point rising with the increase of chlorine until the decachlor compound is reached. Substitution products from these various chlorides are now in preparation.

UNIVERSITY OF MINNESOTA,
MINNEAPOLIS, MINN.

THE PITCH AND THE TERPENES OF THE NORWAY PINE AND THE DOUGLAS FIR.

BY G. B. FRANKFORTER.

Received August 2, 1906.

PRELIMINARY.

IT HAS been known for several years that the Norway pine and the Douglas fir are rich in the terpenes and resin. During a few days in the spring, the Norway pine seems almost as rich in pitch and turpentine as its southern sister species but the conditions are such that "boxing" as practised in the south is out of the question. A series of "boxing" experiments resulted in collecting a considerable quantity of pitch for chemical examination and incidentally proved the impracticability of this method in the north. Although boxing does not seem practicable in the north and west, so far as I have been able to determine, the reason seems to be largely due to climatic conditions so that if the pitch and turpentine of the north and west are to be utilized, other methods than the common method of the south must be employed.

At the present time, nothing has been done by the lumbering industries either in the north or west toward utilizing the large amount of waste pitchy material. As a result, enormous quantities of wood, too rich in pitch to be of any value to the lumbering industries are burned or thrown aside as worthless. The enormous profits in lumber have made it unnecessary for lumbering industries to look to any of the by-products in order to earn large dividends on capital invested. As a natural consequence

no effort has been made by these corporations to utilize the waste products, and to produce pitch and turpentine in the north.

At the present time, practically all the turpentine used in the north and west comes from the south. The small quantity made in the north and west is scarcely worth considering. The tars and resins likewise come almost wholly from the south and from foreign countries. The rapid increase in the demand for these products has increased the already rapid destruction of the forests of the south to such an extent that at the present rate of destruction it is only a matter of a few years when the southern forests will be completely destroyed. This condition of affairs makes it absolutely necessary that new and modern methods of orcharding should be resorted to at once and that new fields should be opened by utilizing the waste products regarded at present as worthless. The United States Department of Agriculture has already fully realized the present conditions and has sounded a warning through one of its officials, Dr. Charles H. Herty, who in an admirable paper on "Turpentine Orcharding," shows that the southern industry will disappear in the near future unless the present methods are radically changed. That new fields may be developed seems both essential and certain, but much pioneer work must yet be done before these new fields become producers of turpentine, colophonium and tar.

This work was begun several years ago with the object of studying the northern turpentine problem from the industrial standpoint and especially with the idea of comparing the products of these hitherto unknown species with those of the south from the chemical point of view. The red or Norway pine, *Pinus resinosa*, and the Douglas fir or spruce, *Pseudotsuga taxifolia*, on account of their abundance, have been taken up first. Other important species will be taken up later.

Both of the above-named species contain considerable pitch but neither will yield an appreciable quantity by the "boxing" method of the south. Of these two species, the Norway comes the nearer to the southern pine, but the fir wood is on the whole a little richer in both resin and in turpentine than the Norway pine.

The Norway Pine.—The so-called "northern pine," or *Pinus resinosa*, is one of the important species of the north. It is one of the two great lumbering species of the northwestern states. The "white pine," the other species, is preferable for lumber on

account of the smaller amount of resin it contains, but the northern pine is sought after because the trees are, as a rule, larger. It very seldom happens that a tree is so full of pitch that it can not be used for lumber, although frequently trees are found to contain so much pitch that the lumber can only be used for certain purposes.

During the past twelve years the problem of recovering the pitch from the Norway pine has been studied. It was found that, during the winter months when the lumbering firms fell most of their timber, the pitch is largely in the lower part of the trunk and in the roots. It seemed, therefore, that the greater part of the pitch might, in some way, be extracted from the stumps and from the waste material in the lumbering business. This has been the prime object of the experiments which are given below.

So far as could be ascertained, the northern pine had not been studied when this work was begun several years ago. Professor Henry Trimble, in a monograph on the pine family, briefly refers to one of the above-named species but no systematic work was done on it further than the study of the twigs and needles together with a brief examination of the wood itself. Nothing definite was known either of the amount of pitch in the wood or of the amount of turpentine in the pitch. Through kindness of the Weyerhauser Lumber Company,[1] the writer was able to obtain a quantity of water-white pitch just as it came from the trees by the "boxing process." This and the pitch obtained from the stumps and other waste material have been examined. The pitch from the stumps was recovered by extraction, by steam distillation and by slow destructive distillation. From these experiments, it is evident that in the near future, these waste products will be utilized, not only in the production of the turpentine but also of tar and other by-products.

Among the problems to be solved were, first the amount of colophonium and turpentine present in the various grades of wood, and second a method for the saving of these products.

That the exact amount of pitch might be ascertained, a large number of determinations were made on the various samples of wood, ranging from the richest to the poorest in pitch. Various

[1] I am especially indebted to Mrs. J. R. Jewett, through whose influence the first Norway pitch was collected in any quantity.

methods were used in the extraction. The following numbers are averages of several determinations each:

Lean wood gave an average of 6.2 per cent. of pitch.

Average wood gave an average of 8.6 per cent. of pitch.

Stumps gave an average of 19.4 per cent. of pitch.

Pitchy wood gave 39.1 per cent. of pitch.

Very pitchy wood gave 42.6 per cent. of pitch.

Properties of Norway Pitch.—Norway pitch obtained from the trees by boxing is colorless and mobile while that obtained from the wood by extraction with the common solvents is slightly colored, otherwise their properties are identical.

Specific gravity of Norway pitch at 20°, 0.8137.

Index of refraction, 1.47869.

Optical activity at 20° is $(\alpha)_D = +4°$.

The pitch as obtained by the above methods of extraction contains about one-fifth of its weight of turpentine, the remainder being colophonium or resin with a very small quantity of water. An average of five determinations gave the following:

Percentage of turpentine, 22.1; percentage of colophonium, 77.3; percentage of water, 0.6.

When exposed to the air the pitch loses turpentine so that after a month or two it becomes a semisolid or solid, depending upon the amount of turpentine remaining.

The colophonium has already been studied and the report on the work will follow this paper.

Fir Wood.—The Douglas fir is to the western states what the Norway pine is to the northern and the yellow pine is to the southern states. The species is interesting on account of the enormous size which it attains and on account of the wide variation in the amount of pitch which it contains. Owing to the high specific gravity of the pitchy wood, a series of specific gravity determinations was made on samples lean and rich in pitch, with the following results:

	Fir.	Norway.
Lean wood, sp. gr. at 20°, average of 5 tests.....	0.6074	0.6025
Medium wood, sp. gr. at 20°, average of 5 tests.....	0.6711	0.6432
Fat wood, sp. gr. at 20°, average of 5 tests.....	0.8225	0.7984
Very fat wood, sp. gr. at 20°, average of 5 tests.....	0.9456	0.9122
Roots (green), sp. gr. at 20°, average of 5 tests.....	0.9746	0.9321

Fir Pitch.—The Douglas fir likewise varies widely in the quantity of pitch. It frequently happens that fir logs are so pitchy

as to be worthless for lumber. They are therefore thrown away or burned. In order to determine the quantity of pitch in various grades of wood, a series of determinations was made by extracting with the various solvents and evaporating so as to avoid loss of the turpentine. The richest and the poorest samples of wood were selected for examination.

An average of five determinations in each of the samples given below, gave the following results:

Very lean wood gave 11.6 per cent. of pitch.

Lean wood gave 13.5 per cent. of pitch.

Medium wood gave 19.8 per cent. of pitch.

Rich wood gave 40.7 per cent. of pitch.

Very rich wood gave 42.4 per cent. of pitch.

Properties of Fir Pitch.—Fir pitch as it runs from the trees is a perfectly clear liquid varying somewhat in its properties. Usually it is water-white and quite mobile. On exposure to the air it changes its color and slowly becomes viscous. This change is due, as in the case of the Norway pitch, to loss of turpentine and to slow oxidation.

The water-white pitch was collected directly from the tree, placed in a closed vessel, so as to prevent oxidation, and kept in this condition until examined. On exposure to the air it was found to change. White pitch had the following properties: It is colorless with a peculiar aromatic odor.

Sp. gr. at 20°, 0.9821.

Index of refraction at 20°, 1.51745.

Optical activity $(\alpha)_D = -8.82$.

At a freezing temperature it is a solid, gradually changing until at 15° it is quite mobile. The amount of turpentine in the fir pitch was about 22 per cent., or the same as in the Norway pitch.

The Terpenes.—The terpenes from the Norway pine and the Douglas fir have been studied. They have been obtained from the pitch which had been recovered by "boxing" and from the pitch which had been extracted from the wood by the various solvents. In addition to these methods, they were obtained from the wood by destructive distillation. In each case it was found that the terpenes obtained by destructive distillation differed from those which were obtained from the wood and from the pitch by steam distillation or by extraction from the wood. Those

obtained from the wood by steam distillation and extraction seem to be of simpler nature than those obtained by destructive distillation. The terpenes obtained by destructive distillation have a wide variation of boiling-points, ranging from 149° to 208°. Even the properties of the compounds of the same boiling-points seemed to have been changed during the process of destructive distillation. The following is a comparison of the two terpenes.

	Norway terpene.		Fir terpene.	
	Steam Dist.	Destructive Dist.	Steam Dist.	Destructive Dist.
Specific gravity at 20°	0.8636	0.8666	0.8621	0.8662
Boiling-point.....	153–154°	158–160°	153.5–154°	157–160°
Index of refraction at 20°...	1.47127	1.4716	1.47299	1.47246
Optical activity.....$(\alpha)_D$ =	+ 17.39	—7.56°	—47.2	—29.4°

These terpenes are now being studied.

UNIVERSITY OF MINNESOTA.

[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE.]

A METHOD FOR THE DETERMINATION OF CITRAL IN LEMON OILS AND EXTRACTS.

BY EDWARD MACKAY CHACE.

Received July 13, 1906.

THE detection of the adulteration of lemon oils and extracts is a problem that has long been disturbing those chemists who are engaged in food and drug analyses. Methods for the detection of the crude forms of adulterations have been devised and are in the main satisfactory. Unfortunately, as the lemon oil industry has developed, certain by-products have come into existence and in the effort to cheapen the cost, these products have been used to produce a grade of impure oil.

With the introduction of these oils the detection of factitious oils and extracts has become a more difficult matter. When the adulteration consisted in the addition of foreign substances such as turpentine or of the substitution of other oils for lemon oil, determinations of the physical constants of the sample and of the first fractions of its distillate were generally sufficient. Now, however, when it consists in varying the proportion of the constituents themselves, physical constants alone are not sufficient.

Lemon oil is composed of 90 per cent. *d*-limonene, 4 to 6 per cent. citral, the remainder being other aldehydes and oxygenated bodies.

It will be readily seen that the physical constants of citral would have to be greatly different from those of lemon oil in order that its partial removal could be detected. As a matter of fact, in their optical activity the two are markedly different, citral being inactive while lemon oil has a rotation of $+60°$ at $20°$. Methods, however, depending upon the polarization of the oil before and after the removal of the citral have not been brought to a satisfactory state of perfection, probably on account of the difficulty of freeing the oil from citral. The citral sulphite compound has a tendency to split up in the presence of the alkali formed in the reaction.

As for chemical methods no satisfactory method has yet been devised for the determination of any of the constituents. Many attempts have been made to perfect methods for estimating citral but all have serious faults affecting their accuracy. Little or no work has been done toward amplification or improvement of the methods on lemon extracts since the work of Mitchell[1] although attention has been called to the need of a method for citral.

The method which is described in the following pages was an attempt toward the determination of citral in lemon oil, but the error made in comparing the solution and standard becomes so great when multiplied to correct for the dilution that it somewhat impairs the usefulness of the method for oils. On extracts the conditions are different and nothing is wanting in the way of accuracy. Medicus in 1895[2] published an article on the determination of aldehydes in distilled liquors, this method depending upon the recoloration of a solution of fuchsin in sulphurous acid. Tolman testing this method while working on whiskies in this bureau discovered that it was essential that the color should be developed at a low temperature.

In modifying the method to admit of its use on lemon oils this fact was verified. It was at first thought that the reagent would have to be made up in alcohol on account of the insolubility of lemon oil. No satisfactory way of preparing an alcoholic reagent was discovered, however. The reagent finally used is similar to that of Medicus but containing a much larger quantity of sulphurous acid. The method as modified is as follows: Reagents, aldehyde, free alcohol 95 per cent. by volume. The alcohol was

[1] This Journal, 21, 1132 (1899).

[2] Forch. Ber. Lebensm. 1895, 299.

allowed to stand over alkali for several days, distilled, and the distillate boiled for several hours under a reflux condenser with 25 grams per liter of metaphenylenediamine hydrochloride and finally distilled. After this treatment it contains only minute traces of aldehydes.[1] Fuchsin solution: Dissolve 0.5 gram of fuchsin in 100 cc. of water and add a solution of sulphurous acid containing 16 grams of sulphur dioxide. Allow to stand until decolorized and make up to one liter. This solution deteriorates on standing and should therefore be made up every two or three days.

Standard citral solution: Dissolve 1 gram of chemically pure citral and make up to one liter with 50 per cent. by volume alcohol. The citral used was obtained from Schimmel & Company, guaranteed chemically pure. Its physical constants corresponded to those of pure citral. Two samples purchased at different times were identical. Manipulation: While in use all reagents were kept in a water-bath cooled to 15°, and all comparison tubes were left in the bath for ten minutes before the comparison was made. A bath such as was described by Given[2] was used.

For lemon oil 2 grams of the sample were weighed and transferred to a 100 cc. flask with alcohol, cooled to 15°, and made up to the mark. For lemon extracts a larger amount was necessary, usually 20 to 30 grams. Aliquot portions of this solution, about 4 cc. measured at the temperature of the bath, were placed in comparison tubes, 20 cc. of the aldehyde-free alcohol added, then 20 cc. of the fuchsin solution and finally made up to 50 cc. with the alcohol. Comparison tubes were prepared in the same way taking 4 cc. of the standard solution. All the tubes, after mixing, were allowed to remain in the bath for ten minutes, when they were removed and the comparisons made either by direct matching or by the use of a colorimeter. When a colorimeter was used which read percentages of color as compared with the standard, a correction had to be made, owing to the fact that the color developed was not proportional to the amount present. This correction varies somewhat with the conditions under which the samples are worked. In order to avoid it, the first sample weighed out was used as a trial estimation, a second sample being used for the correct determination. The amount weighed for this sample was sufficient to give the solution approximately the same strength

[1] For another method see Dunlap: This Journal, 28, 395.

[2] This Journal, 12, 1519 (1905).

as the standard, *i. e.*, 1 mg. citral per cubic centimeter, using the trial determination as a basis for the calculation. The readings on the second sample were usually so close as not to require a correction. Two or three comparisons were made on this solution and the average taken. The color developed by the lemon oil is not exactly the same shade as that developed by citral. This fact may be due to the presence of citronellal, as the color is not altered by the addition of limonene to the standard.

To test the accuracy of the method the following determinations were made. A sample of limonene containing some citral was used as a base and several samples made by adding known quantities of citral. The method was also tried on solutions of citral and on lemon oil. Four determinations were made on the limonene as follows: A, 2.27 per cent.; B, 2.31 per cent.; C, 2.41 per cent.; D, 2.36 per cent.; average, 2.34 per cent. citral. Sample A was composed of 97 grams of the limonene and 3 grams of citral having in all 5.28 grams of citral per 100 grams. Two determinations were made, both giving 5.29 per cent. citral. Sample B contained 5.46 grams of citral in 94.54 grams of citral-free limonene making it contain 5.46 per cent. Four determinations resulted as follows: 5.74, 5.82, 4.90, 4.87 (the poor results here can only be accounted for by the fact that the fuchsin sulphurous acid solution was too old for accurate use). Sample C contained 20.85 grams of a terpene containing 0.25 per cent. of citral or 0.0521 gram, to which were added 1.0075 gram citral, making the oil contain 4.85 per cent. Five determinations gave a minimum of 4.90 per cent., maximum of 5.21 per cent., average 5.05 per cent. Sample D, 97.83 grams limonene containing 0.225 gram citral and 4.63 grams of added citral, the whole containing 7.71 per cent. citral. Three determinations gave 7.61, 7.57 and 7.62 respectively. Sample E was made up of terpenes containing 0.1150 gram of citral and 0.0770 gram of citral, having 3.78 per cent. of the latter. Three determinations resulted as follows: 3.61, 3.84, 3.47, averaging 3.62.

Lemon extracts were made up as follows:

	Gram citral per 100 cc.	Found.
A	0.1065	0.1092
B	0.1060	0.1110
C	0.0968	0.1071
D	0.30	0.282
E	0.12	0.129
F	0.25	0.23

A great many other determinations were made on known samples and as stated above. Satisfactory results were always obtained in the case of lemon extracts, while the results on oils were not so good. The maximum error on oils was usually less than 0.5 per cent. while the average was in the majority of cases within 0.2 per cent.

The essential point to be observed in using the method is to keep the temperature of the reagents and the comparison tubes down to at least 15°, and give the standard and sample exactly the same treatment throughout.

[CONTRIBUTION FROM THE FOOD DIVISION OF THE BUREAU OF CHEMISTRY, U. S. DEPT. OF AGRICULTURE. SENT BY H. W. WILEY.]

ESTIMATION OF SUGARS BY MEANS OF THE REFRACTOMETER.

BY L. M. TOLMAN AND W. B. SMITH.

Received July 13, 1906.

IN A great many materials such as syrups, molasses, and similar substances which are for all practical purposes solutions of sugar and water, the estimation of sugar has long been made by determining the specific gravity with a hydrometer or pycnometer and from the specific gravity calculating the percentage of sugars from a table or by some formula.

This figure, if the solution is a mixture of a pure sugar and water, can be very accurately determined but in syrups and molasses which are impure mixtures, it represents more nearly a determination of the total substances in solution or the total solids. The determination of total solids is a very important one in a great many food products as a check on the other determination and it is for work of this kind that the specific gravity is of value. The accuracy of the specific gravity method in a mixed sugar solution such as we ordinarily have to deal with, depends on the fact that the different sugars have very nearly the same specific gravity for the same concentration. The specific gravity method is also especially useful with substances which are decomposed by drying at a high temperature, such as solutions containing large amounts of invert sugar, where results by drying are too low.

The index of refraction is a figure of practically the same value as the specific gravity in solutions of the kind mentioned above and has about the same limitations. The index of refraction of solutions of soluble carbohydrates increases regularly with the concentration, and the accuracy of the determination is limited only by the accuracy and sensitiveness of the refractometer. Stolle[1] published some results on the index of refraction of sugar solutions using the Pulfrich refractometer and showed that with sucrose, *d*-glucose, *δ-l*-fructose ("levulose") and lactose, there was little variation in the reading of the refractometer with solutions of the same concentration and that very accurate results could be obtained with pure sugar solutions. He also demonstrated that the relation between the index of refraction and specific gravity as calculated by the Lorenz formula $\frac{N_2-1}{(N_2+2)D}$ was a constant, 0.206, thus showing that the same results can be obtained by the index of refraction and the specific gravity.

The following work was undertaken to test the value and accuracy of the Abbé refractometer for this kind of work, to check up Stolle's work, and to complete the list of sugars, as he had no figures on maltose, commercial glucose, or the other soluble component of glucose, that is dextrin, which is often an ingredient of the commercial products on the market.

The instrument used was the new form of the Abbé refractometer with a water-jacket prism so that the temperature at which the readings were made could be exactly regulated. The index of refraction was obtained in exactly the same manner as when an oil is examined in the same instrument.

The instrument was standardized against a quartz plate with a known index of refraction and against pure water and found to read slightly low, about 0.0004, and the readings were corrected by this factor.

The readings were all made at 20°, using ordinary light and compensating for the dispersion by means of the prisms in the instrument. The sugar solutions were made up by weighing the sugars into a glass stoppered flask and then adding a weighed amount of water so that the results were direct percentages by weight.

[1] Z. Ver. deut. Zucker-Ind. 1901, 335–347 and 469–487.

The moisture in the various sugars was determined by drying at 70° to constant weight and at a diminished pressure of about 27 inches. It can be seen that a method of this kind would have many advantages in inspection work—the ease and rapidity with which a determination can be made and the ease and accuracy with which the temperature can be regulated as well as the small amount of sample needed for the determination give it many advantages over the specific gravity method.

The following curve shows graphically the results obtained with the various sugars.

The curve is drawn from the results obtained with sucrose up to a concentration of 65 per cent. from which point it was extended by calculation to 90 per cent. The points for commercial glucose between 80 and 90 per cent. were determined by readings with four different glucoses and they were found to coincide exactly with the calculated curve for sucrose; determinations with glucose of other concentrations, as shown on the curve, also coincide with the sucrose line.

The other sugars examined were maltose and lactose which are also on the sucrose curve, showing that for practical purposes all these sugars have the same index of refraction for the same concentration and that a table prepared for sucrose will be satisfactory for all.

The only other soluble carbohydrate examined was dextrin which, as is shown on the curve, has a slightly higher index of refraction. The close agreement between sucrose and commercial glucose, which is a mixture of dextrose, maltose, and dextrin, is due to the fact that dextrose and maltose have an index of refraction very slightly lower than sucrose while dextrin is slightly higher, the resultant being practically that of sucrose. The following table shows better than the curve, which is not on a sufficiently large scale, the difference between the various sugars.

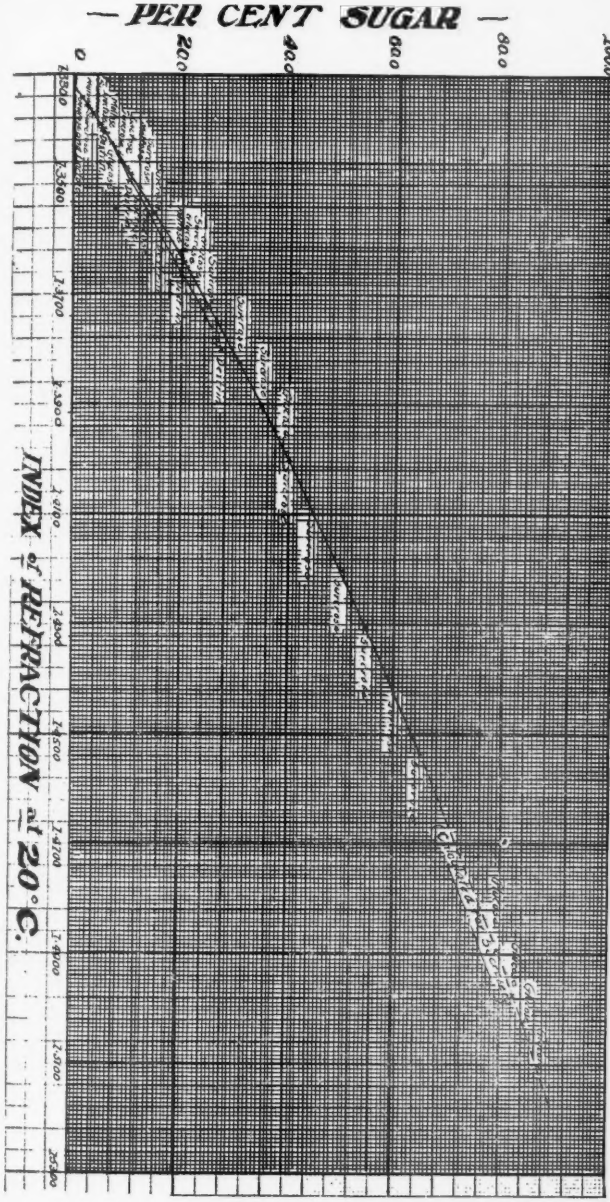

— PER CENT SUGAR —
0
20.0
40.0
60.0
80.0
100.0
INDEX of REFRACTION at 20° C.

TABLE I.—INDEX TO REFRACTION OF VARIOUS SUGARS OF DIFFERENT CONCENTRATION.

Dried in vacuum at 70° C. to constant weight.

Index of Refraction 20° C.	Sucrose. Per cent.	Maltose. Per cent.	Commercial glucose. Per cent.	Lactose. Per cent,	Dextrin. Per cent.	Stolle. *d*-Glucose. Per cent.	Stolle. *δ-l*-Fructose. Per cent.
1.3343	1.00	1.00	1.00	1.00	1.00	1.00	1.14
1.3357	2.00	2.07	2.00	2.00	1.93	1.80	2.07
1.3402	5.00	5.07	5.00	5.13	4.87	5.13	5.13
1.3477	10.00	10.07	10.07	10.13	9.60	10.13	10.13
1.3555	15.00	15.12	15.06	15.13	14.13	15.19	15.19
1.3637	20.00	20.17	20.06		18.94	20.29	20.24
1.3722	25.00		25.00		23.71	25.47	25.47
1.3810	30.00		30.02		28.78		
1.3902	35.00		35.03				
1.3997	40.00		40.05				
1.4096	45.00		45.04				
1.4200	50.00		50.03				
1.4306	55.00		55.02				
1.4419	60.00		60.01				
1.4534	65.00		65.01				
1.4653	70.00		70.00				
1.4776	75.00		75.00				
1.4903	80.00		80.00				
1.5034	85.00		85.00				
1.5170	90.00		90.00				

Taking sucrose as the standard, the other sugars in concentrations up to 20 per cent. show practically no difference in the reading on the refractometer. A reading of 1.3637 is equivalent to 20 per cent. of sucrose, 20.17 of maltose, 20.06 per cent. of commercial glucose, 20.29 per cent. of *d*-glucose, 20.24 per cent. of *δ-l*-fructose and 18.94 per cent. of dextrin. Dextrin alone of all the substances examined differs appreciably from sucrose, it having a slightly higher index of refraction.

The index of lactose is also very close to that of sucrose so that in most cases the same table can be used for all of the sugars in the same way that the Brix table is used for specific gravity determinations. The following table for the value of the index of refraction for sucrose for each per cent. up to 90 per cent. has been calculated from the curve, and for ordinary work this will be found satisfactory for all sugars.

TABLE II.—INDEX OF REFRACTION OF SUCROSE.

Sucrose. Per cent.	Index of refraction 20° C.	Sucrose. Per cent.	Index of refraction 20° C.	Sucrose. Per cent.	Index of refraction 20° C.
1	1.3343	31	1.3828	61	1.4442
2	1.3357	32	1.3847	62	1.4465
3	1.3372	33	1.3865	63	1.4488
4	1.3387	34	1.3883	64	1.4511
5	1.3402	35	1.3902	65	1.4534
6	1.3417	36	1.3921	66	1.4557
7	1.3432	37	1.3940	67	1.4581
8	1.3447	38	1.3959	68	1.4605
9	1.3462	39	1.3978	69	1.4629
10	1.3477	40	1.3997	70	1.4653
11	1.3492	41	1.4017	71	1.4677
12	1.3508	42	1.4036	72	1.4701
13	1.3524	43	1.4056	73	1.4726
14	1.3539	44	1.4076	74	1.4751
15	1.3555	45	1.4096	75	1.4776
16	1.3572	46	1.4117	76	1.4801
17	1.3588	47	1.4137	77	1.4826
18	1.3604	48	1.4158	78	1.4851
19	1.3621	49	1.4179	79	1.4877
20	1.3637	50	1.4200	80	1.4903
21	1.3654	51	1.4221	81	1.4929
22	1.3671	52	1.4242	82	1.4955
23	1.3688	53	1.4263	83	1.4981
24	1.3705	54	1.4284	84	1.5007
25	1.3722	55	1.4306	85	1.5034
26	1.3739	56	1.4328	86	1.5061
27	1.3756	57	1.4351	87	1.5088
28	1.3774	58	1.4373	88	1.5115
29	1.3792	59	1.4396	89	1.5142
30	1.3810	60	1.4419	90	1.5170

In order to correct for different reading temperatures, the following table was prepared, readings being made on the same solutions at 20°, and at 30°, and on concentrations varying from 2 per cent. to 62 per cent.

TABLE III.—CORRECTION FOR TEMPERATURE.

Percentage of sugar.	Index at 20° C.	Index at 30° C.	Difference.	Correction for 10° in per cent. sugar.	Correction for 10° in per cent. sugar, from Brix table.
2.18	1.3358	1.3348	0.0010	0.66	0.64
7.43	1.3438	1.3428	0.0010	0.66	0.67
15.82	1.3569	1.3557	0.0012	0.70	0.70
51.71	1.4236	1.4219	0.0017	0.81	0.79
62.52	1.4477	1.4459	0.0018	0.78	0.76

The differences were calculated to per cent. of sugar and compared with the correction for temperature used in specific gravity work, the Brix table for correction for temperature being used. The results show that the temperature correction for the specific gravity and the index of refraction are practically the same and the table as given for Brix can be used for the index of refraction. The manner of using the table is the same. The reading of index of refraction is made at room temperature and this reading calculated to per cent. of sugar, then the proper correction from the table calculated and applied.

In the Brix table for correction for temperature the maximum correction is at a concentration of about 50 per cent. and, as will be seen from the table above, this same fact is noted in the temperature correction for index of refraction.

In conclusion: It appears from this work that the refractometer is a satisfactory instrument for determining the soluble carbohydrates in solution under the same conditions as those under which specific gravity can be used, and in fact it gives the same results; that it has many advantages over the specific gravity method in speed, ease of manipulation and amount of sample required for the determination; that for a great deal of work where quickness and approximate accuracy only are necessary, the refractometer will be used. The butyro-refractometer is of no value for this work as its range of readings does not take in sugar solutions below 50 per cent. of sugar.

THE OPTICAL ROTATION OF GLIADIN IN CERTAIN ORGANIC SOLVENTS.

By W. E. Mathewson.

Received August 4, 1906.

The experiments given here were carried out in connection with an investigation, the object of which was to effect some improvement on the present methods of flour analysis. The work has been interrupted so it has been thought best to publish these results.

The gliadin used was prepared from a bakers' grade hard wheat flour by extracting with 60 per cent. alcohol, filtering the extract until perfectly clear, concentrating and precipitating with absolute alcohol. The crude gliadin thus obtained was again dissolved and precipitated, digested repeatedly with ether and finally dried

over sulphuric acid. All alcohol and ether used had been carefully redistilled. The preparation was soluble to a perfectly clear and almost colorless solution in dilute alcohol. Duplicate portions contained 17.42 per cent. and 17.52 per cent. of nitrogen, determined by the Gunning method, the digestion being continued for two hours after the mixture had become colorless. It was thoroughly mixed during and after the drying so that the nitrogen determinations might be consistent with the polarimetric observations. It is very probable that the proteid was not quite free from moisture; and the specific rotations obtained have been corrected by multiplying by the factor 1766/1747.

The gliadin was soluble in dilute methyl and propyl alcohols, and in glacial acetic acid, phenol, paracresol and benzyl alcohol. A white precipitate, presumably gliadin, was produced when the phenol solution was treated with ether, acetone or pyridine, and somewhat less readily when treated with benzene or chloroform. Pure methyl, ethyl, propyl and amyl alcohols produced precipitates, the amount required being less, the greater the molecular weight of the alcohol. No turbidity followed the addition of several volumes of aniline, phenylhydrazine, or nitrobenzene, but when gliadin was treated with these substances it did not seem to dissolve, and the clear filtrates showed practically no optical activity. It seemed somewhat soluble in benzaldehyde, but the sample of the latter used was not pure.

In order to ascertain whether the gliadin underwent decomposition on dissolving in phenol, about 7 grams were taken, dissolved in about 100 cc. hot phenol and the solution, after cooling, poured into about 500 cc. pure benzene. A heavy precipitate was produced, although the addition of a little of the supernatant liquid to benzene caused a further separation of solid material, showing that a considerable amount still remained dissolved. The liquid was decanted off, the precipitate washed repeatedly with benzene, drained with suction and dried for three weeks over sulphuric acid *in vacuo*. It still retained a faint odor of phenol. Two portions were taken, dissolved in 70 per cent. ethyl alcohol, and the solutions polarized. The latter were not absolutely clear but were sufficiently clear to enable saccharimeter readings to be obtained without difficulty. Ten cc. were taken from the saccharimeter tube and the nitrogen content determined. From this the specific rotation was calculated, assuming

the gliadin to be equal to the nitrogen multiplied by 10000/1766. The following are the data:

Saccharimeter reading, 40° C. 100 mm. tube.	Grams of nitrogen in 100 cc. at 40° C.	$[\alpha]_D^{40°C.}$
—4.53° V.	0.3051	—90.95
—5.45° V.	0.3678	—90.76

The specific rotation of the substance seems to have suffered but little change. It gave the biuret reaction and the red-purple coloration with diluted sulphuric acid exactly as does pure gliadin. A solution of gliadin in phenol, giving a saccharimeter reading of —19.7° V (200 mm. tube), was sealed up in a glass bulb and maintained at a temperature of about 140° in an air-bath for three and one-half hours. It then gave a reading of —18.4° V.

The solutions of gliadin in glacial acetic acid and in benzyl alcohol gave precipitates with ether exactly resembling gliadin in appearance, and which dissolved readily in dilute alcohol. These latter solutions gave the biuret reaction.

The specific rotations of the gliadin were obtained with a triple shadow saccharimeter, a jacketed tube being used for the solution. The following are the data:

Solvent.	Grams gliadin per cc. at 40°.	Saccharimeter reading in Ventzke degrees.	$[\alpha]_D^{40}$. Degrees.
Methyl alcohol, 70 per cent....	0.03644	—19.81	— 95.3
Methyl alcohol, 70 per cent....	0.03366	—18.42	— 96.0
Ethyl alcohol, 70 per cent.....	0.03085	—16.21	— 92.1
Ethyl alcohol, 70 per cent.....	0.04499	—23.55	— 91.8
Ethyl alcohol, 60 per cent.....	0.02264	—12.52	— 96.9
Ethyl alcohol, 60 per cent.....	0.02388	—13.13	— 96.4
Ethyl alcohol, 60 per cent.....	0.03126	—17.25	— 96.7
Ethyl alcohol, 50 per cent.....	0.02895	—16.29	— 98.6
Ethyl alcohol, 50 per cent	0.04914	—27.55	— 98.3
Propyl alcohol, 60 per cent ...	0.02990	—17.07	—100.9
Propyl alcohol, 60 per cent ...	0.03015	—17.42	—101.3
Phenol, 70 per cent	0.02035	—14.25	—122.7
Phenol, 70 per cent	0.03340	—23.56	—123.6
Phenol, anhydrous.....	0.02824	—21.31	—132.2
Phenol, anhydrous.....	0.03018	—22.73	—132.0
Phenol, anhydrous.....	0.04288	—32.07	—131.1
Paracresol.....	0.02799	—19.54	—121.0
Glacial acetic acid	0.04267	—19.69	— 80.9
Glacial acetic acid	0.05014	—22.48	— 78.6
Benzyl alcohol.....	0.02282	— 6.91	— 53.1
Benzyl alcohol.....	0.03050	—10.14	— 58.3

The methyl and propyl alcohols and the phenol used were the chemically pure grades from well-known manufacturers and were

fractionated before use. The acetic acid and cresol were chemically pure grade but were not further purified. The benzyl alcohol was fractionated. It had a boiling-point of about 202° (uncorrected). The aromatic compounds were tested for optical activity.

The divergence in the results obtained with the benzyl alcohol is doubtless due to the decomposition of a part of the proteid by the heating necessary to bring it into solution. The sample giving the lower reading was purposely kept at a high temperature considerably longer than the other to see if the rotation would be markedly changed. Doubtless the other determinations are also affected with some error due to the same cause, although this was guarded against as far as was practicable.

The fact that gliadin is soluble in phenol would seem to render possible an approximate determination of its molecular weight by the freezing-point method. Since it is also soluble in boiling 70 per cent. propyl alcohol, a determination by the boiling-point method might be made since G. N. Lewis has shown[1] that Raoult's law regarding the elevation of the boiling-point can be applied to a binary solvent whose vapor has the same percentage composition as the liquid. The presence of traces of moisture would affect the results by the latter method much less, although gliadin is doubtless more or less altered by continued warming with any solvent containing water.

An attempt has been made to estimate the gliadin present in flour by digestion with phenol and polarization of the filtered extract. The results obtained seem to indicate that a quite complete extraction of the gliadin is effected. It is possible, however, that more or less glutenin also dissolves in the phenol. The chief difficulty encountered is in the filtration of the mixtures.

[CONTRIBUTION FROM THE U. S. DEPARTMENT OF AGRICULTURE, BUREAU OF CHEMISTRY. SENT BY H. W. WILEY.]

THE SEPARATION OF PROTEOSES AND PEPTONES FROM THE SIMPLER AMINO BODIES.

BY W. D. BIGELOW AND F. C. COOK.

Received June 30, 1906.

OF THE methods that have been employed during recent years for the separation of proteoses and peptones from the simpler

[1] This Journal, **28**, 766.

amino bodies, the following methods have been used most commonly.

First, Stutzer's method[1] by means of precipitation with phosphotungstic acid.

Second, Mallet's method[2] by precipitation with phosphotungstic acid in hot solutions.

Third, Allen and Searle's method[3] by precipitation with bromine.

Fourth, Schjerning's method[4] by precipitation with a tannin salt solution.

It was believed by Stutzer that the method proposed by him separated peptones completely from all of the simpler amino bodies. Since that time it has been shown repeatedly that phosphotungstic acid precipitates some of the meat bases and that the reagent is not suitable for the purpose for which it was first suggested.

The bromine method of Allen and Searle[5] has been shown to be utterly untrustworthy. It decomposes both proteids and meat bases with the liberation of nitrogen. It has been shown by the writers[6] that bromine does not precipitate all of the proteid bodies present, that the amount precipitated under varying conditions is not constant, and that it is possible to so fix the conditions that relative amounts can be secured. It is true that the results are greatly improved by forming the bromine precipitate in the filtrate from the proteoses precipitated by zinc sulphate, the filtrate being diluted with an equal volume of water before precipitation with bromine. Even then, however, the results obtained by the method are far from satisfactory in the presence of a considerable amount of simple amino bodies.

In previous work[7] the writers found the tannin salt method of Schjerning to have some advantages in this separation. Our work with this method, however, has indicated that slight changes of conditions produced marked influences on the results, and it seemed important to study the method with a view to determining whether it were not possible to so fix conditions as to obtain re-

[1] Z. anal. Chem. 34, 568 (1895).
[2] U. S. Dept. Agr., Bureau of Chem., Bull. 54.
[3] Analyst, 22, 258 (1897).
[4] Z. anal. Chem. 39, 545 (1900).
[5] U. S. Dep't. Agr., Bureau of Chem., Bull. 73.
[6] Ibid., Bull. 81.
[7] Ibid., Bull. 90.

sults that were more nearly correct, or at any rate relatively constant. As a result of this work it was found that much more satisfactory and more constant results were obtained by increasing both the tannin content and the salt content of the reagent. Further particulars of our study of the method are given later.

COMPARISONS OF THE ACTION OF REAGENTS ON MEAT BASES.

Solutions of a number of simple amino bodies were treated with phosphotungstic acid in hot and cold solutions; with the tannin-salt reagent of the strength previously employed by the writers; and also a stronger tannin salt solution which was found to give more complete precipitation of the proteid bodies. The results of this work are given in Table I.

By consulting Table I it will be seen that with the more dilute tannin salt solution, precipitates were obtained with creatine, trimethylamine and phenylenediamine. These results were confirmed with the stronger solution of tannin salt, except that no precipitate was given with trimethylamine when the stronger solution was used. The weaker solution also gave a slight turbidity, but insufficient to indicate the precipitation of a determinable amount of nitrogen with glycocoll, alanine, glutamic acid, creatine and glutamine. It is probable that failure to obtain this turbidity with the stronger tannin salt solution is due to the increased difficulty of detecting a turbidity in that solution, and not to the solvent action of the stronger solution on the slight amount of material precipitated by the more dilute solution. Considering the fact that this turbidity was not detected in the stronger solution, and therefore at least was not increased by increasing the strength of the reagent, it is suggested that this was due not to the insolubility of the amino bodies in question in the presence of the tannin salt solution, but rather to a small amount of impurity contained in the preparations examined. It is apparent, however, that creatine and phenylenediamine cannot be separated by this method from peptones. In the case of creatine this is a serious matter, since that substance is the meat base which occurs most abundantly in meat and meat extract.

The error due to creatine, however, can be eliminated by determining the amount of creatine present before and after the pre-

TABLE I.—ACTION OF PROTEID PRECIPITANTS ON AMINO BODIES.

Amino body.	Tannin salt.[1]	Tannin salt.[2]	Phosphotungstic acid, cold.	Phosphotungstic acid, hot (96° C.).
Glycocoll.	Cloud.	None.	None.	None.
Alanine.	Cloud.	.....	None.	None.
Creatine.	Slight ppt.	Rather heavy ppt.	White granular ppt.	None.
Glutamic acid.	Cloud.	None.	None.	None.
Aspartic acid.	None.	None.	None.	None.
Allantoin.	None.	None.	None.	None.
Asparagine.	None.	None.	None.	None.
Betaine.	None.	.....	Flaky white ppt.	None.
Creatinine.	Slight turbidity.	None.	White granular ppt.	None.
Glutamine.	Cloud.	None.	None.	None.
Guanine.	None.	None.	None.	None.
Xanthine.	None.	.....	None.	None.
Hypoxanthine.	None.	.....	White granular ppt.	None.
Leucine.	None.	None.	None.	None.
Trimethylamine.	Heavy ppt.	None.	White ppt.[3]	None.
Diphenylamine.	None.	.....	None.	None.
Phenylenediamine.	Black flaky ppt.	Brown flaky ppt.	A heavy white ppt.	Brownish ppt.
Acetamide.	None.	None.	None.	None.
Sarcosine.	.....	None.	.....	

[1] Four grams of sodium chloride and 10 cc. of 12 per cent. tannin per 100 cc.

[2] Fifteen grams of sodium chloride and 20 cc. of 12 per cent. tannin per 100 cc.

[3] This disappeared on standing 2 or 3 minutes.

cipitation with the tannin salt reagent. The method for this determination is described below. It is believed that phenylenediamine does not occur in meat extract, and that in the examination of meat products, the fact that this substance is precipitated by the tannin salt reagent may be disregarded.

Mixtures of the amino bodies mentioned above were also treated with the same reagents except that in this case the stronger tannin salt solution was not employed, the work having been completed and our samples of amino bodies exhausted before our results indicating the advisability of using the stronger tannin salt solution were obtained. The results obtained by treating the mixtures of amino bodies with the reagents mentioned, as given in Table II, confirm those obtained with the unmixed solutions.

TABLE II.—ACTION OF PROTEID PRECIPITANTS ON MIXTURES OF AMINO BODIES.

Amino bodies.	Tannin salt.[1]	Phosphotungstic acid. Cold.	Phosphotungstic acid. Hot (96° C).
Leucine Glycocoll	Very slight cloud.	None.	None.
Aspartic & glutamic acid.	Slight cloud.	None.	None.
Acetamide Betaine	None.	None.	None.
Creatine Creatinine	Slight cloud.	Heavy white ppt.	None.
Allantoin Asparagine	None.	None.	None.
Xanthine Hypoxanthine	Faint cloud.	Heavy white ppt.	Slight ppt.
Guanine Glutamine	None.	None.	None.
Trimethylamine Diphenylamine	Heavy yellow brown ppt.	Granular white ppt.	Granular white ppt.

Mixtures were then prepared of two commercial products—Witte's peptone and somatose—consisting largely of proteoses and peptones—with a number of the simple amino bodies, and treated with the reagents mentioned above. The nitrogen was determined in all solutions from which these mixtures were prepared, and the amount of nitrogen contained in the proteose or peptone body and in the simple amino bodies, as well as the

[1] Four grams of sodium chloride and 10 cc. of 12 per cent. tannin per 100 cc.

This disappeared on standing 2 or 3 minutes.

amount of nitrogen precipitated by the reagent employed, are given in Table III.

TABLE III.—NITROGEN PRECIPITATED BY PHOSPHOTUNGSTIC ACID AND ZINC SULPHATE FROM MIXTURES OF WITTE'S PEPTONE OR SOMATOSE AND AMINO BODIES.

Nitrogen contained and determined.	Witte's peptone. Gram.	Witte's peptone, leucine and tyrosine. Gram.	Leucine and tyrosine precipitated. Gram.	Witte's peptone. Gram.	Witte's peptone, glycocoll, creatine and creatinine. Gram.	Glycocoll, creatin, and creatinine precipitated. Gram.
Nitrogen content of Witte's peptone or somatose	0.0714	0.0714	.....	0.0762	0.0762	.....
Nitrogen content of solution of amino bodies	.....	0.0045[1]	.....	.....	0.0171	.....
Nitrogen precipitated by phosphotungstic acid	0.0655	0.0683	0.0028	0.0695	0.0790	0.0095
Nitrogen precipitated by zinc sulphate	0.0404	0.0407	0.0003	0.0498	0.0475	.....

Nitrogen contained and determined.	Somatose. Gram.	Somatose, glycocoll, leucine, tyrosine, xanthine, hypoxanthine and guanine. Gram.	Glycocoll, leucine, tyrosine, xanthine, hypoxanthine, and guanine precipitated. Gram.	Somatose. Gram.	Somatose, glycocoll and glutamine. Gram.	Glycocoll and glutamine precipitated. Gram.
Nitrogen content of Witte's peptone or somatose	0.0619	0.0619	.....	0.0619	0.0619	.....
Nitrogen content of solution of amino bodies	.....	0.0106	.....	.....	0.0129	.....
Nitrogen precipitated by phosphotungstic acid	0.0594	0.0637	0.0043	0.0585	0.0604	0.0019
Nitrogen precipitated by zinc sulphate	0.0545	0.0547	0.0002	.....	.....	.....

The amount of nitrogen in the portion of Witte's peptone solution taken for examination was 0.0714 gram. Of this amount phosphotungstic acid (Stutzer's method) was found to precipitate 0.0655 gram, and zinc sulphate precipitated 0.0404 gram. To a similar portion of the solution of Witte's peptone was added a solution of leucine and tyrosine containing 0.0045 gram of nitrogen. Of this mixture phosphotungstic acid precipitated 0.0683 gram of nitrogen, and zinc sulphate precipitated 0.0407 gram of nitrogen. The precipitate obtained with zinc sulphate indicates that about two-thirds of the nitrogen present in this sample consisted of

[1] Leucine 0.0025 gram and tyrosine 0.0020 gram.

proteoses. Practically all of the remaining third is probably peptones. By deducting 0.0655 from 0.0683 the amount of nitrogen in the form of leucine and tyrosine precipitated by phosphotungstic acid is given as 0.0028 gram. The results given in this table appear to confirm the qualitative results given in Tables I and II.

ACTION OF TANNIN SALT REAGENT ON MEAT BASES IN THE PRESENCE OF PROTEOSES AND PEPTONES.

The tannin salt reagent was not included in Table III as at the time the work forming the basis of that table was done we had not satisfied ourselves with regard to the conditions under which the method could best be conducted. Similar work with the tannin salt reagent was repeated at a later time, and the results are given in Table IV.

TABLE IV.—NITROGEN PRECIPITATED FROM MIXTURES OF SOMATOSE AND MEAT BASES BY TANNIN SALT REAGENT.[1]

Substance.	Nitrogen in somatose used. Grams.	Nitrogen in amino bodies used. Grams.	Total nitrogen precipitated. Gram.	Amino nitrogen precipitated. Gram.
Blank	0.1006	none	0.0966	none
Phenylenediamine	0.1006	0.0230	0.1040	0.0074
Creatine	0.1006	0.0494	0.1080	0.0114
Creatinine	0.1006	0.0090	0.0984	0 0018
Glycocoll	0.1006	0.0202	0.0966	none
Sarcosine	0.1066	0.0270	0.0956	—0.0010
Allantoin	0.1006	0.0348	0.0994	0.0028
Leucine	0.1006	0.0034	0.0966	none

Quantities of 0.8 gram each of somatose were mixed with several of the more important meat bases, and the nitrogen determined in the material precipitated by the tannin salt reagent from the mixture. The reagent employed for this purpose was the stronger solution mentioned above; that is, it contained 10 grams of sodium chloride and 4 grams of tannin per 100 cc. of the solution in which the precipitation occurs. The temperature was 12° C.

It will be seen that in only two cases was an appreciable quantity of nitrogen obtained in the precipitate in excess of that obtained with the somatose alone. In the presence of phenylenediamine this was equal to 0.0074 gram of nitrogen, or about one-third

[1] Reagent employed contained 10 grams of sodium chloride and 4 grams of tannin per 100 cc. of the solution in which the precipitation occurred. The temperature was at 12° C.

of the amount present in the amino body. In the presence of creatine containing 0.0494 gram of nitrogen, a little less than one-fourth of that amount, or 0.0114 gram of nitrogen was precipitated by the reagent. In the case of the other amino bodies studied the nitrogen in the precipitate from the tannin salt reagent was so nearly equal to that of the blank that it may be ignored as due to inaccuracies of the method.

NITROGEN PRECIPITATED BY VARYING QUANTITIES OF SALT AND TANNIN.

In the presence of a considerable amount of precipitable matter it is impracticable to determine with accuracy the quantity of reagent necessary to make precipitation complete. The amount of reagent was accordingly varied through wide limits for the purpose of determining the amount with which the most complete precipitation of proteid bodies could be obtained. It was found that by increasing the salt solution, even at a concentration far below that at which the precipitation of the ordinary proteids with sodium chloride occurs, the amount of nitrogen precipitated by the tannin salt solution was largely increased. It was also found that a corresponding increase of the precipitate was obtained by increasing the amount of tannin in the solution.

The varying results obtained with different strengths of sodium chloride and tannin suggested the advisability of determining whether there was any degree of concentration for both salt and tannin at which slight changes in concentration would be without material influence upon the results. To determine this the amount of nitrogen precipitated by the tannin salt reagent was determined in solutions whose sodium chloride content varied from 0.8 to 26 grams per 100 cc., and whose tannin content varied from 1.25 to 10 grams per 100 cc.

An inquiry of this sort is greatly complicated, owing to the fact that pure solutions of the proteid bodies can not be obtained. We have found it necessary to study those conditions which would give the maximum results with as pure solutions as were obtainable of proteoses and peptones, and then to use under such conditions solutions of the various meat bases in order to determine whether the latter were precipitated thereby.

An inspection of Tables V and VI will show that approximately the maximum results were obtained by using about 15 grams

per 100 cc. of sodium chloride and 4 or 5 grams per 100 cc. of tannin; that is, the proteid bodies under examination are dissolved in a small amount of water and concentrated solutions of sodium chloride and tannin added in sufficient amount to form solutions of the concentration given above. It also appears from Tables V and VI that a considerable excess of tannin may be employed without any tendency of the reagent to dissolve the precipitate formed in excess.

It is, of course, impossible to determine how completely peptones are precipitated by the tannin salt reagent. It is interesting to know, however, that 15 grams of sodium chloride and 4 or 5 grams of tannin per 100 cc. of solution, which gives the maximum precipitation of proteids, precipitates from 96 to 98 per cent. of the total nitrogen contained in somatose, which from the nature of its preparation is supposed to consist largely of albumoses with a small amount of peptone. With the same reagent we precipitated about 94 per cent. of the total nitrogen contained in Witte's peptone, which is also supposed to consist chiefly of albumoses and peptones, but to contain a larger percentage of peptones than is found in somatose.

It thus appears that maximum precipitations of proteoses and peptones can be obtained from these substances with tannic acid and sodium chloride in the proportion of from 4 to 5 grams of the former and 15 grams of the latter per 100 cc. of the solution in which the precipitation is effected. This, taken into consideration with the fact that minimum precipitations are produced by this reagent with the meat bases, indicates that satisfactory results may be obtained with the reagent.

EFFECT OF TEMPERATURE ON PRECIPITATION.

Aliquot portions of solutions containing proteoses, peptones, and simple amino bodies were precipitated with the tannin salt reagent at three temperatures:

First, in a refrigerator at about 12° C.

Second, at room temperature, the precipitate standing over night at about 23° C.

Third, in a drying oven heated with a thermostat, the temperature regulated at about 40° C.

It was found that higher results were obtained with a lower temperature and that the nitrogen precipitated at room tem-

TABLE V.—AMOUNT OF NITROGEN PRECIPITATED FROM ARMOUR'S EXTRACT (TOTAL NITROGEN IN 20 CC. = 0.1780 GRAM) BY VARYING AMOUNTS OF TANNIN AND SALT.

(Ice box temperature, 12° C., total volume, 100 cc.)

Sodium chloride per 100 cc. Grams.	Grams of tannin in varying amounts of 12 per cent. solution used.										
	10 cc. = 1.25 grams. Gram.	15 cc. = 1.87 grams. Gram.	20 cc. = 2.50 grams. Gram.	25 cc = 3.12 grams. Gram.	30 cc. = 3.75 grams. Gram.	35 cc. = 4.37 grams. Gram.	40 cc. = 5 00 grams. Gram.	50 cc. = 6.25 grams. Gram.	60 cc. = 7.50 grams. Gram.	70 cc. = 8.75 grams. Gram.	80 cc. = 10.00 grams. Gram.
1	0.0831	0.0856	0.0899	....	0.0921	....	....	....	....	....	0.0959
3	0.0819	0.0878	0.0900	....	0.0927	....	....	....	....	....	....
5	0.0809	0.0868	0.0887	....	0.0909	....	....	0.0951	....	....	0.1015
7	0.0825	0.0878	0.0921	....	0.0964	....	....	....	....	....	....
8	0.0826	0.0868	0.0909	....	0.0909	....	....	....	....	....	....
9	0.0831	0.0872	....	....	0.0965	....	....	....	....	....	....
10	0.0825	0.0873	....	....	0.1191	....	....	0.0997	....	....	....
11	0.0847	0.0906	0.0921	....	0.0983	....	....	....	....	....	....
13	0.0847	0.0884	....	....	....	....	....	....	....	....	....
15	0.0847	0.0896	0.0923 0.0937	0.0937	0.0950 0.0999	....	0.1036	....	0.1009	0.1043	0.1083
17½	....	....	0.0939	0.0982	0.0985	0.0982	0.1070	0.1051	0.1087	....	....
20	....	0.0928	0.0967 0.0971	....	0.1013	....	0.1060	0.1109	....	....	....
22	....	....	0.0985	0.1010	....	....	....	....	....	....	....
23	....	....									
25	....	0.0980	0.1021	....	0.1079	....	....	....	....	....	....

[1] From this point on in the majority of cases a 24 per cent. solution was used diluted one-half, the resulting strength being the same as that indicated in the table.

TABLE VI.—AMOUNT OF NITROGEN PRECIPITATED FROM 1 GRAM OF SOMATOSE (VARYING AMOUNTS OF TANNIN AND SALT.

[Temperature 12° C; total volume 100 cc.]

Sodium chloride per 100 cc.	10 cc. = 1.25 grams.	15 cc. = 1.87 grams.	20 cc. = 2.50 grams.[1]	25 cc. = 3.12 grams.	30 cc. = 3.75 grams.	35 cc. = 4.37 grams.	40 cc. = 5.00 grams.
	Grams of tannin in varying amounts of 12 per cent. s						
Grams.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.	Gram.
0.8.....	**0.1014**	**0.1081** 0.1111	**0.1086** 0.1126	.....	**0.1092** 0.1152	.....	.....
1.0.....	.....	.....	.....	.....	.....	.....	.....
2.0.....	.....	.....	.....	.....	.....	.....	.....
4.0.....	.....	**0.1036** 0.1063	**0.1097** 0.1137	.....	**0.1097** 0.1157	.....	.....
5.0.....	**0.1036**	.....	.....	.....	.....	.....	.....
6.0.....	.....	.....	.....	.....	.....	.....	.....
7.0.....	0.1067	0.1133	0.1149	.....	**0.1109** 0.1169	.....	.....
8.0.....	0.1073	0.1127	**0.1114** 0.1149	.....	0.1151	.....	.....
9.0.....	**0.1070**	**0.1109** 0.1139	.....	.....	.....	.....	.....
10.0.....	0.1079	0.1133	0.1137	.....	**0.1120** 0.1151	.....	.....
11.0.....	0.1083	0.1145	0.1155	.....	0.1163	.....	.....
12.0.....	0.1101	0.1145	**0.1120** 0.1160	.....	0.1163	.....	.....
13.0.....	0.1095	**0.1140** 0.1155	0.1155	.....	0.1169	.....	.....
14.0.....	**0.1060**	**0.1125**	.....	.....	0.1192	.....	.....
15.0.....	0.1095	0.1149	0.1188 0.1171	0.1191	0.1199 0.1175	0.1208	0.1211
16.0.....	.....	.....	**0.1125** 0.1165	.....	.....	.....	.....
17.0.....	.....	**0.1125** 0.1155	0.1188	0.1191	0.1199	0.1202	0.1205
18.0.....	**0.1098**	.....	.....	.....	.....	.....	.....
20.0.....	0.1148	0.1183	0.1193 0.1186	0.1191	0.1199 0.1208	0.1202	0.1219 0.1217
23.0.....	.....	0.1184	0.1199 0.1186	0.1202 0.1209	0.1217[2]	.....	.....
25.0.....	.....	.....	0.1200	.....	.....	.....	.....
26.0.....	.....	.....	0.1187	.....	.....	.....	.....

[1] From the column headed "20 cc." on, in the majority of cases a 24 per cent. sol ing strength being the same as that indicated in the table.

[2] Twenty-eight cc. of tannin used.

NOTE—The figures in ordinary type are those of the regular series in which the undetermined. The figures in black-faced type do not belong to the regular series. In all used was determined. The fact that these figures are lower than those of the regula the nitrogen in the tannin, as well as to the fact that a different lot of tannin was used

ED FROM 1 GRAM OF SOMATOSE (TOTAL NITROGE
AMOUNTS OF TANNIN AND SALT.

ture 12° C; total volume 100 cc.]

nnin in varying amounts of 12 per cent. solution used.

30 cc. = 3.75 grams. Gram.	35 cc. = 4.37 grams. Gram.	40 cc. = 5.00 grams. Gram.	50 cc. = 6.25 grams. Gram.	60 cc. 7.50 gram Gram
0.1092 0.1152	.....	.....	.....	.....
.....	.....	.....	0.1167	0.117
.....	.....	.....	.....	0.116
0.1097 0.1157	.....	.....	.....	0.117
.....	.....	.....	low 0.1127	.....
.....	.....	.....	.....	0.117
0.1109 0.1169	.....	.....	0.1169	.....
0.1151	.....	.....	0.1141	0.118
.....	.....	.....	.....	.....
0.1120 0.1151	.....	.....	0.1189	0.1195
0.1163	.....	.....	0.1147	0.1207
0.1163	.....	.....	0.1153	.....
0.1169	.....	.....	0.1147	0.1207
0.1192	.....	.....	0.1153	.....
0.1199 0.1175	0.1208	0.1211	0.1209	0.122
.....	.....	.....	.....	.....
0.1199	0.1202	0.1205	0.1211	0.121
.....	.....	.....	.....	.....
0.1199 0.1208	0.1202	0.1219 0.1217	0.1217 0.1212	.....
0.1217[2] 0.1209	.....	.....	.....	.....
.....	.....	.....	.....	.....
.....	.....	.....	.....	.....

majority of cases a 24 per cent. solution was diluted t
table.

e of the regular series in which the nitrogen in the tan
t belong to the regular series. In all of these cases the n
are lower than those of the regular series is due to th
at a different lot of tannin was used.

L NITROGEN = 0.2149 GRAM) BY

used.

c. = 25 ms. am.	60 cc. = 7.50 grams. Gram.	70 cc. = 8.75 grams. Gram.	80 cc. = 10.00 grams. Gram.
...	.....	.....	.....
167	0.1173	.....	0.1157
...	0.1161	0.1167	.....
...	0.1179	0.1179	.....
127	.....	.....	.....
...	0.1179	0.1167	.....
169	.....	.....	.....
141	0.1189	0.1185	.....
...	.....	.....	.....
89	0.1195	0.1189	0.1207
47	0.1207		
53	.....	.....	.....
47	0.1207	.....	0.1219
53	.....	.....	.....
..	.....	.....	.....
09	0.1223	0.1223	0.1229
..	.....	.....	.....
11	0.1212	0.1207	.....
..	.....	.....	.....
17	.....	.....	.....
12			
..	.....	.....	.....
..	.....	.....	.....
..	.....	.....	.....

as diluted to one-half, the result-

in the tannin solution used was
cases the nitrogen in the tannin
is due to the allowance made for

perature was greater in amount than that precipitated at 40° C. Moreover, the lower the temperature, the clearer was the supernatant liquid and the more complete the precipitation. The supernatant liquid in the case of the precipitations made at 40° C. was quite commonly turbid, and in many cases filtration was entirely impracticable. In the case of the precipitations made at room temperature the supernatant liquid, though usually clear, was occasionally turbid and filtration difficult. With the precipitations made in the refrigerator at a temperature of about 12° C. the supernatant liquid was almost always clear and the filtrations (which were also conducted in the refrigerator) rapid and satisfactory, leaving a perfectly clear filtrate.

COMPARISON OF VARIOUS TANNINS.

Different samples of tannin do not give uniform results with a given mixture of proteids and meat bases. The difference in some cases is so great as to lead to considerable inaccuracy, and it is of course essential that a uniform tannin be used in the prosecution of any particular investigation. At the same time there has been nothing in our experience to indicate that this difference is so great as to preclude the practicability of comparing in a general way the work of different laboratories. The lack of uniformity is considerable, however, and impairs the value of such a comparison. The results of this study are given in Tables VII and VIII. One important consideration that appears to have been overlooked is the nitrogen content of tannin. As will be seen in Table VIII the amount of nitrogen contained

TABLE VII.—COMPARISON OF THE PRECIPITATING POWER OF TWO TANNINS ON 1 GRAM OF SOMATOSE IN THE PRESENCE OF VARYING AMOUNTS OF SALT.

Tannin solution.	Sodium chloride. Per cent.	Nitrogen precipitated. Gram.	Difference in nitrogen precipitated. Gram.
A[1]	7	0.1127	0.0026
B[2]	7	0.1153	
A	10	0.1132	0.0021
B	10	0.1153	
A	15	0.1143	0.0026
B	15	0.1169	
A	20	0.1159	0.0022
B	20	0.1181	

[1] Nitrogen per 10 cc. = 0.0020 gram.

[2] Nitrogen per 10 cc. = 0.0012 gram.

in some samples of tannin is considerable, and a correction must always be made. A varying amount of the nitrogen in the tannin is either insoluble in water, or is precipitated from a tannin solution by sodium chloride, and hence is insoluble in the tannin salt reagent. It is important that blanks be run with the reagents employed, and that a correction be made for the total nitrogen in the tannin employed as well as the nitrogen in the tannin insoluble in the tannin salt reagent.

In Table VIII are given the results of the influence of reagents prepared from three samples of tannin upon solutions of somatose. In all cases the volume of the liquid in which the precipitation occurred was 100 cc., and contained 2.49 grams of tannin and 10 grams of salt. In the three samples the amount of nitrogen varied from 0.1155 to 0.1191 gram. The nitrogen content of the tannin itself must also be taken into consideration. This is a factor which we have only recently considered in connection with this work, but the amount of nitrogen has been found so great that it should always be determined and a correction applied. The three samples mentioned were found to contain 0.0007 to 0.0052 gram of nitrogen in 20 cc. of the sample.

TABLE VIII.[1]—NITROGEN CONTENT AND COMPARISON OF PRECIPITATING POWER OF VARIOUS TANNINS.

Reagent.	Total nitrogen. Gram.	Nitrogen precipitated. Gram.[2]	Nitrogen in the 2.49 grams of tannin used. Gram.
No. 1 Tannin	0.1249	0.1191	0.00068
No. 2 Tannin	0.1249	0.1165	0.00112
No. 3 Tannin	0.1249	0.1155	0.0052
No. 4 Tannin	0.1249	.....	0.0104

To further study this question the nitrogen precipitate was obtained on quantities of 1 gram of somatose, using the tannin salt precipitate prepared from two of the above lots of tannin. The results are given in Table VII. In all cases the precipitations occurred in 100 cc. of liquid, which contained 12 grams of tannin and the amount of sodium chloride given in the table. It will be seen that the difference in precipitating power of the two tannins is of considerable magnitude. In all cases in both Tables VII and VIII the quantity of nitrogen contained in the tannin itself

[1] All tannin solutions were made 12 per cent. and 20 cc. used in each case. Ten grams of salt were also added and 1 gram of somatose used. Ice box temperature, 12°.

[2] Corrected for nitrogen content of reagent.

has been allowed for, and is not responsible for the difference shown in the precipitating power of the various tannins.

PRESERVATION OF TANNIN SALT REAGENT.

It is well known that tannin undergoes fermentation in solution and loses to a large extent its power of precipitating proteids. We have found that this occurs even in the presence of a considerable quantity of salt, and that the tannin salt reagent should be kept in a cool place, and should not stand more than a few days before using.

DETAILED DESCRIPTION OF MODIFIED TANNIN SALT METHOD.

One gram of meat powders, 2 grams of preparations of pasty consistency and from 10 to 20 cc. of liquid or semiliquid extracts should be employed. Solid and pasty preparations are dissolved in a little cold water in a 100 cc. graduated flask, keeping the volume within 20 cc.

Then 50 cc. of a solution containing 30 grams of sodium chloride per 100 cc. are added and the flask agitated to insure the thorough mixing of its contents and the solution of the sample. The flask is now placed in the ice box at approximately 12° C. After the solution has reached the ice box temperature (this requires an hour usually) 30 cc. of a 24 per cent. solution of tannin (which must be at ice box temperature) are added. The total volume is now diluted to 100 cc. The contents of the flask are thoroughly mixed and the flask returned to the ice box, where it remains over night. In the morning the solution is filtered at ice box temperature into a 50 cc. graduated flask. The nitrogen is determined in this filtrate, and also in an aliquot portion of the filtrate from a blank, in which the reagents alone are employed. The nitrogen found in the 50 cc. portion multiplied by two (after correction for the nitrogen in the blank) gives the total nitrogen in the filtrate, and includes the nitrogen present as ammonia and all of the nitrogen of the meat bases except that portion of the creatine precipitated by the tannin salt reagent.

In the examination of products that contain insoluble or coagulable proteids, 20 cc. of the filtrate from the coagulable proteids are used for this determination. The volumes of the solution of the meat extract employed, and of the two reagents will then make 100 cc. and require no further dilution. The nitrogen thus precipitated by the tannin salt reagent (calculated

by difference) consists of that present in the form of proteoses and peptones, and the peptone nitrogen may of course be found by deducting the proteose nitrogen, obtained by precipitation with zinc sulphate, from the total amount of nitrogen precipitated by the tannin salt reagent.

DETERMINATION OF CREATINE AND CREATININE.

It is stated above that the error occasioned by the precipitation of a portion of the creatine by the tannin salt reagent may be corrected by determining the creatine before the application of the tannin-salt reagent, and in the filtrate from the precipitate given by that reagent. At the suggestion of Prof. L. B. Mendel the method of Folin[1] for the determination of creatine in urine was applied by us to the determination of creatine in meat extracts. Before applying the method it was of course necessary to convert the creatine present into creatinine by dehydrating with hydrochloric acid. As we have noted above, the tannin salt reagent precipitates a portion of the creatine in mixtures of albumoses, peptones and creatine. This is also the case in meat extracts and the proportion of creatine precipitated by the tannin salt reagent varies with each individual extract, as one would suppose. It was therefore necessary to determine the total creatinine (after dehydrating with hydrochloric acid) in the original sample, and also in the peptone filtrate, the difference being the creatine precipitated by the tannin salt reagent. In making the creatine determination on the original sample, a portion of the filtrate from the coagulable and insoluble proteids was employed. The amount used corresponded to about 2 grams of the original solid extract. In the case of the peptone filtrate some trouble was experienced, as the tannin which was present in large quantities interfered and it was necessary to remove it. The following method of procedure was consequently adopted:

From 40 to 50 cc. of the tannin salt filtrate was heated on the steam-bath with hydrochloric acid to convert all creatine to creatinine, 5 cc. of 10 per cent. barium chloride solution were added and sodium hydroxide to distinct alkalinity. The contents of the flask were then thoroughly mixed by shaking, filtered, and the precipitate washed with water. From the filtrate and washings, which are now practically free from tannin, the excess of

[1] Z. Physiol. Chem. 10, 391, 1886.

barium is removed by precipitation with sulphuric acid, filtered, and the precipitate washed. The filtrate is now ready for the usual application of the creatine method. When very small quantities of creatine are present, the usual difficulties of reading are experienced, but in most cases the readings ran from 2 mm. to 12 mm. on the Duboscq colorimeter. The percentage of peptones as determined is corrected by the figure thus obtained. It is of course necessary to determine ammonia in the original sample and make a correction therefore in the calculated percentage of peptones.

THE PHOSPHORUS CONTENT OF FECES FAT.[1]

By J. H. Long and W. A. Johnson.

Received July 13, 1906.

In a recent communication[2] attention was called by one of us to the high phosphorus content of the feces fat of a man in normal health, under conditions where, according to the usual statements in the literature, little or no phosphorus should be found. The phosphorus, in the form of phosphoric acid, obtained from feces fat, as extracted by perfectly dry ether, has always been assumed to have its origin in bodies of the lecithin type, and the detection and estimation of lecithin here have been made to depend on the recognition and determination of phosphoric acid among the products of decomposition of the fat.

However, that all the ether-soluble organic phosphorus obtained through the extraction of dried feces may be assumed to come from a lecithin body may well be doubted, in view of the many conflicting results obtained in the last few years in the examination of fresh animal and vegetable tissues as well as of feces. All the more recent investigations on the subject agree in suggesting that what has been called "lecithin" is evidently a mixture, and as a preliminary to the discussion of the nature of the phosphorus-containing bodies in the feces we have thought it well to make a new series of phosphorus, and also nitrogen determinations in the fat extracted under certain conditions.

In the paper cited above the method of extracting the fat was referred to. In the work below the same plans were followed,

[1] Presented at the June (1906) meeting of the American Chemical Society at Ithaca.

[2] Long: This Journal, 28, 704.

but in one case when a large quantity of the fat was desired, the dried mass was rubbed up with fine crushed quartz and extracted in the Soxhlet apparatus in the usual manner. The ether used in the extractions was carefully purified and finally distilled from sodium. The evaporation of the ether after extraction left a crude fat which was purified by dissolving in dry ether, filtering from a slight residue always left and evaporating again. This treatment would exclude inorganic substances, and anything above a trace of glycero-phosphoric acid, if present. The direct ignition of some of the fat thus purified left always a minute amount of residue of phosphate or phosphoric acid. On igniting the fat in the usual manner with sodium or potassium nitrate and carbonate the whole of the phosphorus was left as alkali phosphate which was always determined by the Pemberton method.

The table following gives the results obtained from the feces of seven individuals in normal health living on an ordinary mixed diet. There are also given, in No. 8, the results for nitrogen and phosphorus in the feces of the same man from whom sample No. 3 was obtained at an earlier period.

No. of sample.	Solids.	Per cent. of fat in dry material.	Per cent. of P_2O_5 in fat.	Per cent. of N in fat.	Per cent. of P in fat.
1.....	15.03	8.60	1.02	....	....
2.....	24.25	14.01	1.77	....	....
3.....	28.00	19.45	2.32	....	....
4.....	21.99	18.63	1.05	....	....
5.....	20.00	9.50	0.20	....	....
6.....	24.90	14.12	0.80	....	....
7.....	28.00	15.15	1.20	....	....
8.....	....	16.60	3.66	0.47	1.59

Extreme variations are shown in the percentage amounts of phosphoric acid recovered from the fat. As found before, these amounts are not increased by prolonged extraction. It will also be noted that these results are very high in samples Nos. 3 and 8, which, as mentioned, were from the same individual. It should be stated, in addition, that the very high phosphorus content referred to in our earlier paper was found in feces fat from the same man. As yet we have not been able to discover an explanation for this peculiarity.

All the results in the above table are relatively high and if calculated to ordinary lecithin it is plain that the lecithin content of normal human feces must be considered as high instead of

low as frequently stated. Some references to this subject may be found in the excellent book by Schmidt and Strasburger[1] where certain authorities are quoted. It must be remembered that 1 per cent. of phosphorus corresponds to 26 per cent. of distearyl lecithin, or 1 per cent. of P_2O_5 to over 11.3 per cent. of the same complex fat. The relations for the other possible lecithins are not greatly different. On the assumption that this phosphorus content is due to a pure lecithin solely, and that no other soluble nitrogen compounds are present, a check on the phosphorus content would be secured through a determination of the nitrogen. In ordinary distearyl lecithin the nitrogen and phosphorus stand to each other in the ratio 14:31, but the above table shows a phosphorus percentage much higher than this. The discrepancy may be due to the presence of other bodies, containing nitrogen or phosphorus, or both, in the ether extract, or it may be due to variations in the composition of lecithin itself. Wintgen and Keller[2] give some figures for lecithins prepared from soy beans, and purified by acetone precipitation, in which the nitrogen content is relatively high, in some cases 50 per cent. higher than could correspond to a simple formula, while the phosphorus content is low. It is evident that under the name "lecithin" a number of substances are included which may be only remotely related to bodies of the simple distearyl lecithin type, and for the present we can do no better than refer to them as *lecithans* or, less distinctively, as *phcsphatides* as suggested by several writers. There is a very considerable literature on the occurrence and nature of these bodies, the extent of which may be gathered from recent papers by Schulze and Winterstein,[3] and Koch and Woods.[4] It may be well to recall that Thudichum,[5] in discussing the organic phosphorus compounds of the brain and other organs of the body, described a number of substances, which he classed as phosphatides, in which the phosphorus and nitrogen ratios were quite variable. Some of these bodies appeared to contain two atoms of phosphorus in the molecule. In other compounds he found a great excess of nitrogen, from which the ratio of N:P appeared

[1] "Die Faeces des Menschen," p. 160.

[2] Abs. Biochemisches Centralblatt, 5, 272 (1906).

[3] Z. physiol. Chem. 40, 101 (1903).

[4] J. Biol. Chem. 1, 203 (1906).

[5] Thudichum: "Die chemische Konstitution des Gehirns des Menschen und der Thiere," Tübingen, 1901.

to be 4:1 instead of 1:1, as in the simple lecithins. Quite recently Winterstein and Hiestand[1] have described a new group of vegetable products which appear to consist of a combination of a lecithin and a carbohydrate. Former investigators had included this with the lecithins of low phosphorus content, but the authors now point out the true relation of these bodies.

However, we are not now concerned with the question of the variation in the composition of these lecithin bodies, but with that of their occurrence in the fat of feces. There can be two general sources for these phosphorus-containing fats. They may represent unchanged substances from the original animal or vegetable foods, or they may represent products of metabolism within the human body. Probably each source contributes a share, but if we consider a large fraction as coming from the food it will be necessary to assume that lecithins are more resistant to the digestive operations than are the other fats since the proportion found in the feces fat is relatively higher. The behavior of the lecithin fats in this respect has been pointed out by Stassano and Billon.[2] Estimating from the phosphorus content about 4 grams daily of lecithin in the feces would be indicated by the maximum of the results in the table above, while the other results are much lower. From a vegetable diet alone it is scarcely possible to account for this largest value, but from a mixed diet containing eggs the difficulty is less. But a large part of the crude fat of the feces is known to have other origin than that of the original food directly. Some comes from the destruction of the tissues lining the intestinal tract, some from the bile and some from the bacteria of the intestine. The importance of the bile in this respect has been generally overlooked, since the older analyses in general placed the organic phosphorus content very low. But the investigations of Hammarsten[3] on the biles of different animals have placed the matter in a new light. Hammarsten shows that a very considerable portion of the alcohol-soluble fraction of the bile solids may be classed in the lecithin or "phosphatide" group. The phosphorated fat found in the bile must have its origin in the

[1] Z. physiol. Chem. 47, 496 (1906).

[2] Jahresbericht über die Fortschritte der Thier-Chemie, 33, 76 (1903).

[3] See, especially, article in the Ergebnisse der Physiologie, 4, 1 (1905); "Zur Chemie der Galle."

disintegration of liver tissue, the lecithin content of which is relatively high.

It must be remembered, further, that bacterial cells make up a considerable fraction of the dried feces. Nothing very definite is known of the fat content of the intestinal bacteria, but of certain bacteria from other sources it has been shown that the fat content is high. This is especially true of the tubercle bacillus,[1] but of the minute composition of such fats not much is given in the literature. In view, however, of the general nature of bacterial cells it is fair to assume the presence of lecithin-like bodies in their fat.

Since numerous investigations of recent years have shown the great importance of the lecithins in relation to problems of nutrition, metabolism, and immunity, we have undertaken a continuation of this work with the hope of defining more closely the nature of the phosphorus compounds in the feces fat.

NORTHWESTERN UNIVERSITY MEDICAL SCHOOL,
CHICAGO, July, 1906.

DISCOLORATION OF FRUITS AND VEGETABLES PUT UP IN TIN.

BY F. A. NORTON.

Received July 19, 1906.

A NUMBER of cases of discoloration of fruits and vegetables put up in tin have come to the attention of the writer. In most cases the discoloration was undoubtedly due to sulphides of the heavy metals, the discoloration in some cases being confined to the container, in others affecting the fruits and vegetables as well. The source of the hydrogen sulphide varied in different cases. Some micro-organisms are capable of evolving hydrogen sulphide through breaking down of proteid matter, but this would result only with goods which were not properly sterilized and is not so frequent as some other causes. Also such goods are unfit for consumption so that the discoloration is of minor importance. In other cases hydrogen sulphide resulted from the use of sulphites in connection with fruits, reaction having taken place between the sulphites and vegetable acids with the liberation of sulphurous acid, which, acting upon the tin of the container, had produced

[1] See among other authorities, De Schweinitz: This Journal, 25, 354 (1903).

hydrogen sulphide. Another source of hydrogen sulphide was the decomposition of proteid matter through the use of an exceptionally heavy process by the action of steam under pressure on the proteids. Where discoloration had taken place in the goods, the source of the heavy metals was the tin plate and solder of the container.

All fruits and vegetables, as has been shown by Leach,[1] have a greater or less solvent action upon the tin plate and solder of the container, taking up variable amounts of tin and lead, the extremely acid fruits, like rhubarb, being most active, though some of the vegetables, such as squash and pumpkin, take up very large amounts of tin.

Having pointed out the source of the heavy metals and the hydrogen sulphide, one can very readily understand how the discoloration of these goods would take place. A history of some cases in point will best illustrate the different forms of discoloration.

Recently, some badly discolored pears were sent in to the laboratory for examination. On opening the can a heavy brownish black deposit was discovered over the inside of the can, and wherever the pears came in contact with the can there was also the same deposit on the fruit, rendering it unsightly and unfit for the market. Previous experience by the director of the laboratory, Mr. E. W. Duckwall, at once suggested that sulphites had been used in the preparation of the fruit, and that the discoloration was probably due to their use. Determinations for sulphites were made and they were found to be present in very large quantity. The character of the discoloration, which almost assumed the form of a deposit, suggested to us that it was due to metallic sulphides, principally tin sulphide, resulting from the reaction between the sodium sulphite, vegetable acids and tin.

In order to ascertain whether this was the case or not, pieces of pear of good color were placed in two beakers with pieces of tin and solder in each. To one sodium sulphite was then added and the other simply left in water. The pear not treated with sodium sulphite kept its color perfectly on standing in contact with the tin and solder, but the pear in the beaker to which sulphites had been added soon began to darken, and in the course of two or three days the same brownish black appearance observed in the

[1] "Food Inspection and Analysis," p. 696.

discoloration of the pears in the case at hand had permeated nearly the whole pear tissue of the sample under treatment in the beaker. Some of the brownish deposit, also some of the discolored fruit from the can showing the discoloration, was treated with strong hydrochloric acid, which immediately destroyed the discoloration of the pear tissue and brought the deposit into solution. On diluting, filtering and precipitating with hydrogen sulphide, a small quantity of tin sulphide was obtained, which indicated that the discoloration was due to sulphide of tin and other metallic sulphides. This was further confirmed by treating the inside of the discolored can in which the pears had been put up with strong hydrochloric acid, and testing the fumes given off with lead acetate paper for hydrogen sulphide. A very positive reaction was obtained for sulphides, which was confirmed by other tests. In fact, the odor of hydrogen sulphide evolved from the decomposition of the sulphides seemed to be unmistakably present. This experimental data seemed to show conclusively to us that the discoloration was due to metallic sulphides resulting from the hydrogen sulphide which had been liberated by reaction between the sulphites and the tin, aided by the fruit acids present.

To further test this view pieces of tin foil were treated with sodium sulphite and also with sulphurous acid solution. The tin foil in the sulphurous acid solution quickly became discolored with a considerable brown deposit, which was shown to be tin sulphide, while that in the sulphite solution remained perfectly bright. This would indicate that there would not be much danger of discoloration from reaction between sulphites and tin in a neutral medium, but that where sulphurous acid would be liberated discoloration would be very sure to result.

Other pieces of tin foil were then treated in beakers with sodium sulphite solution to which various acids, such as acetic, lactic, tartaric, citric and others, had been added. In each case discoloration resulted, showing that the vegetable acids had liberated sulphurous acid, which in turn reacted with the tin to form tin sulphide, giving the discoloration. Most fruits contain appreciable amounts of such acids as citric and malic acid. In some cases, where fermentation has taken place to any extent, acetic or lactic acid is present, and fruits or vegetables containing any

of these organic acids, if treated with sulphites, are very sure to produce discoloration.

Soldering fluxes sometimes are somewhat acid, and if a little excess is used, permitting the acid to come in contact with the goods, if these are treated with sulphites, discoloration is very sure to be observed at points where the acid has come in contact with the fruit or vegetable. While it would seem that sulphites can be used without any danger of discoloration in neutral substances, there certainly is much danger of discoloration if they are used in products of a somewhat acid character put up in metal containers.

Discoloration from hydrogen sulphide evolved through the employment of a heavy process is illustrated by the following case: In order to secure the proper cooking of the large siftings of peas, which was not readily accomplished in the blancher, the packer had lengthened the process to fifty-five minutes at 240°, with the result that this pack of peas contained a very large percentage of cans containing discolored peas, while the smaller siftings of peas given a shorter process were free from the discoloration. An examination of the peas in the containers showed the cans to be very much discolored, the inside of the can being of a brownish-purple color, though there was nothing in the nature of a deposit. The discoloration of the peas was confined more particularly to those around the outer portion of the can and the discoloration did not extend into the peas to any great extent. Some of the more badly discolored peas were separated out and a determination of tin made, which was found to be present in considerable quantity. Also the discoloration, both of the peas and the can, was soluble in strong hydrochloric acid, which would be the case with tin sulphide. Reactions for hydrogen sulphide were obtained from the inside of the can quite readily, both with lead acetate paper and sodium nitroprussiate. This same discoloration of the can is noticeable wherever a heavy process is employed and had previously been found by the writer to react for sulphides, evidently being due to tin sulphide formed through hydrogen sulphide liberated during the processing. There is seldom discoloration of the contents, but in this case it seemed that sufficient hydrogen sulphide had been liberated, together with the tin and lead taken up by the contents of the can, to produce the discoloration. Experiments which have been made

show that when proteid substances are acted upon by steam under pressure ammonia and hydrogen sulphide are split off from the proteid molecule, with the formation of albumose and peptone. Dr. Long, in his recent work[1] in his discussion of proteid substances, gives special attention to the decomposition of proteid substances by steam under pressure, stating that if the temperature is high enough the reaction will extend even beyond the formation of ammonia and hydrogen sulphide, resulting in the complete destruction of the proteid molecule. This would explain the source of the hydrogen sulphide, and, taking into consideration the fact that tin and some lead would have been taken up by the peas, would explain the discoloration of the goods.

In order to assure ourselves that sufficient hydrogen sulphide would be produced under a very heavy process to cause the discoloration, two glass jars were filled with peas and to one 50 mg. of stannous chloride were added, and both were processed at 240° for an hour. The peas in the jar to which the tin chloride had been added showed a very marked brown discoloration, from which the other peas were entirely free, which would confirm our findings in this case.

In some cases, especially in corn, we have encountered a discoloration which was more local in character than in the case of the peas just described. In this case the discoloration was confined almost entirely to the vicinity of the seams and cap. As corn is a very stable product and does not change its position in the can it would appear that the discoloration in this case had come more particularly from the solder or from an excess of flux. It has been shown that where a poor grade of solder containing a large amount of lead is used, the action of the fruit or vegetable juice is greater, more metal being brought into solution. Also if an excess of soldering flux, especially if somewhat acid in character, should remain along the seam, it would result in more of the metal of the container being taken up by the contents of the can at those points, and then on liberation of hydrogen sulphide during the process discoloration would result at these points, while the contents of the can otherwise would be free from discoloration.

From the above, it can be stated that sulphites should not be used with goods of an acid character which are to be put up in tin.

[1] "Physiological Chemistry," p. 74.

Where a heavy process is necessary, care should be exercised to avoid the use of an excess of flux or the use of low-grade solder or tin plate which would tend to increase the amount of heavy metals taken up by the goods. Also the length of the process, in order to avoid evolution of hydrogen sulphide, should be as short as possible, consistent with complete sterilization of the goods.

NATIONAL CANNERS' LABORATORY,
ASPINWALL, PA.

NOTES.

Note on the Insolubility of Ferric Hydroxide in Ammoniacal Solutions.—Some years ago difficulty was experienced in this laboratory from the very considerable solubility of ferric hydroxide in an excess of commercial ammonia. It was found, however, that if, after precipitation, the excess of ammonia was expelled by heating upon a steam-bath, the iron was precipitated quantitatively. No experiments were performed at the time to determine the nature of the substance which caused the difficulty, but since it was assumed that similar impurities were likely to be contained by any commercial ammonia, the precaution of precipitating iron with the smallest possible excess of ammonia and of expelling the greater part of this slight excess upon a steam-bath before filtration, has been rigorously followed since the time when the difficulty was first encountered.

The experiments described below were directed to determine, if possible, the extent of this solubility as well as its cause. Solutions of ferric chloride containing about 0.25 gram of iron were precipitated with redistilled laboratory ammonia. In different experiments both hot and cold solutions of the ferric salt were employed, and both a large and a small excess of ammonia. In every case filtration, without suction, was carried out immediately after precipitation. It was considered unnecessary to wash the precipitate. The filtrates were evaporated to small bulk and were then tested for the presence of ferric iron by adding hydrochloric acid (free from iron) and potassium sulphocyanate. Although in every case an extremely slight yellow color was produced, by comparison with standard tubes containing known quantities of iron it was determined that the amount of iron in the filtrate was never as much as one one-hundredth of a milligram.

A repetition of these experiments with commercial ammonia which had not been redistilled gave similar results.

Since it was probable that an excessive amount of amines in the ammonia might influence the solubility of the ferric hydroxide, further experiments were performed in which there was added to the ammonia before precipitation from 1 to 3 grams of the hydrochloride of an amine. The hydrochlorides used were those of methylamine, ethylamine, diethylamine, isoamylamine, ethylenediamine, aniline and phenylhydrazine. As before, in different experiments with the same amine, precipitation was carried out both in hot and in cold solution, and with large quantities of ammonia as well as with a small excess. The filtrates were evaporated to small bulk and tested for ferric iron. In a few cases the filtrate was slightly yellow after evaporation, owing to organic matter, but in these cases the greater part of the color was removed by heating with a considerable quantity of iron-free nitric acid. In the experiments with aniline and phenylhydrazine the oxidizing effect of ferric iron was avoided by nearly neutralizing the ferric solution with ammonia before the addition of the hydrochloride.

The largest quantity of iron found in any one of these filtrates was five one-hundredths of a milligram and in most cases the amount did not exceed one one-hundredth of a milligram. A quantity of precipitate as small as this might well have been mechanically dragged through the filter-paper. At all events the error introduced by the use of an excess of ammonia in precipitating ferric hydroxide is much smaller than the other errors incidental to a quantitative filtration, and the expulsion of the excess of ammonia, at the risk of solution of a portion of the precipitate through hydrolysis of the ammonium salts, should be omitted.

Evidently, the solubility of ferric hydroxide in ammonia which was previously observed was caused by the presence of some organic impurity of unusual occurrence in ammonia.

GREGORY PAUL BAXTER AND ROBERT ARNOLD HUBBARD.

HARVARD UNIVERSITY, CAMBRIDGE, MASS.

July 24, 1906.

A New Qualitative Test for Calcium.—The difficulty of testing for calcium in the presence of barium and strontium, led the

writer to turn his attention to a test for this metal which would not be answered by barium and strontium.

In this connection the action of potassium ferrocyanide has been tried with surprisingly good results. so good in fact, that it seems almost impossible that the reaction has not been used before, in this connection.

As only one reference could be found to the action of potassium ferrocyanide on calcium compounds,[1] the fear of repetition is braved and the test described, in the hope that it may prove useful.

In separating barium, strontium and calcium, the commonly accepted method seems to be precipitation with ammonium carbonate in ammoniacal solution, solution of the washed precipitate in acetic acid, removal of barium by potassium chromate or bichromate, reprecipitation of strontium and calcium by ammonium carbonate in ammoniacal solution, re-solution of the precipitate in acetic or hydrochloric acid, removal of strontium by ammonium sulphate and finally testing for calcium by addition of ammonium oxalate in ammoniacal solution.

The weak point in this scheme is the danger of traces of barium and strontium remaining in solution, with the well-known effect on the calcium test.

The suggested procedure is the same as the foregoing, up to the point of the re-solution of the precipitate after barium has been removed, (except that acetic acid only should be used).

At this point the solution is divided and calcium sulphate added to one portion to test for strontium.

To the other portion, an equal volume of ammonium chloride is added and a few cubic centimeters of potassium ferrocyanide. The presence of calcium is indicated by the formation of a light yellowish green precipitate.

The sensitiveness of the test has been tried on standard solutions of calcium salts and when applied directly to the calcium solutions was found to indicate 1 part of calcium in 7,000 parts. The ammonium oxalate test was also tried and was found to indicate 1 part in 140,000 parts.

The oxalate test was also applied to a series of standard calcium solutions to which strontium had been added. The strontium was removed by ammonium sulphate as in the first method out-

[1] Prescott and Johnson, 1903, p. 212.

lined. Under these conditions the addition of ammonium oxalate caused no precipitate in solutions more dilute than 1 part in 14,000.

The difference is accounted for by the fact that the ammonium sulphate precipitates out a large amount of calcium with the strontium, and by the fact that calcium oxalate is probably more soluble in ammonium sulphate than in water.

The ferrocyanide test was also tried in the regular scheme of analysis and clearly indicated 1 part in 7,000. This 1 part in 7,000 seems to be the solubility limit of the calcium-potassium ferrocyanide.

Under similar conditions and within the limits of the ferrocyanide test, the volume of the precipitate is about four times as great with ferrocyanide as with oxalate.

It might be added that comparatively fresh solutions of potassium ferrocyanide seem to give the best results.

FRED F. FLANDERS.

STATE COLLEGE OF WASHINGTON,
PULLMAN, WASH.

Note on the Coloration of Didymium Glass by Radium Chloride.—About six-tenths of a gram of radium chloride, 7,000 activity, were sealed in a small tube of didymium glass and allowed to remain six months. The colorless glass acquired an exquisite pink color. Unfortunately on analysis, the glass was found to contain manganese. No variation in the absorption spectum of the glass was observed after the exposure. No electrical or sparking effects were noted when the tube was opened.

Note on the Preparation of Rubber Samples for Analysis.—In the course of construction of the buildings of the College of the City of New York, the writer has had to pass upon a number of items involving large contracts. Among these were rubber and cable insulations. The analysis of rubber and insulating material at best is not attended with satisfaction. To eliminate at least one source of error we desired the sample in a pulverulent condition. This was accomplished by thorough chilling with liquid air and grinding under that refrigerant in an ample agate mortar. The analyses were made by Dr. L. H. Friedburg, of this department.

CHAS. BASKERVILLE.

COLLEGE OF THE CITY OF NEW YORK.

On the Liberation of Formaldehyde Gas.—After the article by myself and Mr. West, which appeared in the September number of the Journal, was in press, a paper by Daniel Base appeared (August number of this Journal, page 964) on "Formaldehyde Disinfection and Determination of the Yield of Formaldehyde in Various Methods of Liberating the Gas for the Disinfection of Rooms," in which the process of liberating formaldehyde by means of potassium permanganate has been studied. The results obtained by Base are somewhat different from those given above. The authors of this paper have tried apparatus practically the same as that described by Base, but discarded it as unsatisfactory on account of the large amount of formaldehyde left in the residue, as is indicated by Base's analyses. In fact, unsatisfactory results were obtained in all of the numerous experiments where permanganate alone, either crystal or powdered, was used. The best results with pure permanganate were obtained by the use of a calorimeter bomb as a generator. The permanganate in powdered form was placed in the bomb and by means of an electric appliance the formaldehyde was allowed to drop on the permanganate. The increase in the amount of formaldehyde liberated was undoubtedly due to the heating of the bomb, thus driving off more of the formaldehyde than in an ordinary glass generator. A slight increase in the amount of formaldehyde was likewise obtained by bringing the formaldehyde solution in contact with the permangaate in the bomb under diminished pressure. The percentage of formaldehyde liberated in each case, however, was considerably lower than the percentage obtained by mixing the permanganate with sand. G. B. FRANKFORTER.

NEW BOOKS.

LES INDUSTRIES DE LA CONSERVATION DES ALIMENTS. PAR X. ROCQUES. Paris: Libraire Gauthier-Villars. 1906. xi + 506 pages, 114 figures, 15 fr.

This book is of special interest to those who wish to follow the commercial processes of preparing all forms of preserved and canned foods for the market. The author treats of these processes in a clear and comprehensive manner, using well-selected illustrations wherever necessary.

A brief historical sketch is first given, showing the progress of food preservation processes since the 17th century, calling special

attention to the epoch-making discovery in 1804 by Appert of the efficacy of canning, and to the studies of Liebig, Masson, Pasteur and others.

Then follows a general discussion of the causes and effects of decomposition in foods, with a theoretical resumé of the phenomena of putrefaction. Considerable attention is given to preservation by heat and to a practical treatment of the canning industry, the general technique of canning various fruits and vegetables as well as of fish, meats, meat products and milk being given in detail.

Preservation by cold is treated in a separate chapter dealing with the question of cold storage as applied especially to meat, fruits, fish, eggs and dairy products. Preservation by desiccation follows, with commercial methods for the drying of the various foods to which the process is applicable.

The chapter on food preservation by antiseptics is of paramount interest, on account of the increased use in recent years of chemical preservatives in foods. While discussing the relative efficiency of the various commonly used antiseptics, the author unqualifiedly and justly condemns the use of these substances in food, with the possible exception of sulphurous acid in wine, the use of which, under certain restrictions in the wine industry, has in his opinion been justified to some extent by long practice.

The final chapter on the preservation of eggs is fairly complete and timely.

It is to be regretted that the usefulness of the book is restricted by the lack of an alphabetical index. ALBERT E. LEACH.

THE ELEMENTS OF CHEMICAL ENGINEERING. By J. A. GROSSMAN, with a preface by SIR WM. RAMSAY. London: Chas. Griffin & Co. Philadelphia: J. B. Lippincott & Co. viii + 152 pp. Price, $1.50.

So far as it goes this is a good book but it certainly does not contain sufficient to convert the average graduate in chemistry into an engineer. The book describes and figures the technical equivalents of the beaker, flask, condenser, fractioning tube, air-bath, blowpipe, crucible, funnel, mortar and measuring vessel. There are chapters on the steam boiler and other sources of power; on the application of heat; on the materials used; on technical research and the designing of plant.

The first thing a chemical engineer must do is to design, lay out and build his building. Little will be found here to help him.

Then he must put in shafting, pulleys and belts, without help so far as this book is concerned. The treatment given to the subjects chosen is also too brief, sometimes apparently from lack of information, as important types are not even mentioned. The book is characterized by diffuseness; what is wanted is specific information in short crisp sentences. Chemical engineering is a large subject. To get even an elementary treatise within 500–600 8vo pages it will be necessary to make every word count.

It may be somewhat doubtful whether any one person can be found able to write a satisfactory treatise, which had better be the result of coöperation from several well versed in different phases of the subject. EDWARD HART.

DIE CHEMISCHE REICHSANSTALT VON WILHELM OSTWALD Leipzig 1906

In this pamphlet of twenty-eight pages, after narrating how the plan of a National Bureau of Chemistry took form, Ostwald explains how university laboratories of chemistry are so well organized for instruction as not to be well fitted for some of the most important kinds of chemical research.

The leaders of chemical science in Germany assumed that the proposed laboratory should provide for research in pure chemistry and in applied chemistry, but the technical chemists desired no such concession in the name to their supposed interests, and the new institution, if established, is to be *die chemische Reichsanstalt*, and not *die chemisch-technische Reichsanstalt*. Four divisions are proposed, one for inorganic chemistry including determinations of atomic weight; a second for analytical chemistry; a third for organic chemistry; and a fourth for physical chemistry. For the foundation of such an institution, chemical manufacturers in Germany are ready to provide considerable sums.

Ostwald mentions the fact that part of the activity of our National Bureau of Standards coincides with that of the proposed *chemische Reichsanstalt*. EDWARD W. MORLEY.

RECENT PUBLICATIONS.

FIRST STAGE INORGANIC CHEMISTRY. By G. H. Bailey. Edited by William Briggs. Fourth Impress. (Third Edition). London: Clive. 1906. 264 pp. 2/.

URIC ACID. By A. Haig. London: Churchill. 1906. 2/6.

MANUFACTURE OF LUBRICANTS, SHOE-POLISHES AND LEATHER DRESSINGS. By R. Brunner. London: Scott. 1906. 184 pp. 7/6.

PLACE CHEMISTRY MUST TAKE IN PUBLIC ESTEEM. By H. E. Armstrong. London: Sherratt. 1906. 40 pp. -/6.

RESEARCHES ON CELLULOSE. By C. F. Cross and E. J. Bevan. London: Longmans & Co. 1906. 7/6.

PRESERVATIVES IN FOOD AND FOOD EXAMINATION. By J. C. Thresh and A. E. Porter. London: Churchill. 1906. 500 pp. 14/.

LEATHER MANUFACTURE. A PRACTICAL HANDBOOK OF TANNING, CURRYING AND CHROME LEATHER DRESSING. By A. Watt. Edition Five. London: Lockwood. 1906. 500 pp. 12/6.

HANDBUCH DER ORGANISCHEN CHEMIE. DRITTE AUFLAGE. ERGÄNZUNGSBD. By F. Beilstein. Hamburg: (L. Voss). 1906. 16+1218 pp. Marks 38-.

CHEMISCHES PRAKTIKUM FÜR STUDIERENDE DER NATURWISSENSCHAFTEN. QUALITATIVE ANALYSE. By Max Dittrich. Heidelberg: C. Winter. 1906. 8+216 pp. Marks 5-.

LEHRE VON DER REAKTIONSBESCHLEUNIGUNG DURCH FREMDSTOFFE (KATALYSE). By W. Herz. Stuttgart: F. Enke. 1906. 42 pp. Marks 1.20.

KURZE ANLEITUNG ZUR CHEMISCHEN UNTERSUCHUNG VON ROHSTOFFEN UND PRODUKTEN DER LANDWIRTSCHAFTLICHEN GEWERBE UND DER FETTINDUSTRIE. SECOND EDITION. By Wilhelm Kalmann. Wien: F. Deuticke. 1906. 9+153 pp. Marks 4-.

ELEKTROLYTISCHE ALKALICHLORIDZERLEGUNG MIT FLÜSSIGEN METALLKATHODEN. By R. Lucion. Halle: W. Knapp. 1906. 8+206 pp. Marks 9-.

DIE ÄTHERISCHEN OELE. By F. W. Semmler. Second Volume. Leipzig: Veit & Co. 1906. Marks 33.50.

DER FABRIKCHEMIKER, SEINE AUSBILDUNG UND STELLUNG. By L. Wohlgemuth. Halle: W. Knapp. 1906. 36 pp. Mark 1-.

DIE BRAUNKOHLENTEER-INDUSTRIE. By Ed. Graefe. Halle: W. Knapp. 1906. 8+108 pp. Marks 3.60.

LEHRBUCH DER ANORGANISCHEN CHEMIE. By H. Erdmann. Fourth Edition. Braunschweig: F. Vieweg. 1906. 26+796 pp. Marks 15- (Bound Marks 16-).

HANDBUCH DER ANORGANISCHEN CHEMIE. (In 4 Bdn). Hrsg. von A Abegg. III. Bd. 1. Abtlg. Die Elemente der 3. Gruppe des period. Systems. Leipzig: S. Hirzel. 1906. 10+466 pp. Marks 19-.

UEBER DIE VOLUMETRISCHE BESTIMMUNG VON ORGANISCHEN SULFHYDRATEN UND THIOSÄUREN. By Pet. Klason and Tor Carlson. Uppsale. (Berlin: R. Friedländer & Sohn). 1906. 6 pp. Marks 60-.

ZUR KENNTNIS DER THIOGLYKOLSÄURE. By Pet. Klason and Tor Carlson. Uppsale. (Berlin: R. Friedländer & Sohn). 1906. 9 pp. Marks 60-.

IM VOREXAMEN. 1300 FRAGEN AUS DEM GEBIETE DER ANORGAN. UND ORGAN. CHEMIE..... By Gust. Meyer. Hildesheim: L. Steffen. 1906. 179 pp. Marks 2.50.

LECONS SUR LA PRODUCTION ET L'UTILISATION DES GAZ PAUVRES. By L. Marchis. Paris: H. Dunod et E. Pinat. 1906. 354 pp. 12 francs.

COURS DE CHIMIE ORGANIQUE. By F. Swarts. Paris: A. Hermann. 1906. 700 pp. 15 francs.

L'OZONE. By E. Guarini. Paris: H. Dunod et E. Pinat. 1906. 24 pp. 2 francs.

LA TEINTURE. By E. Chappat. I: Historique, Substances. Paris: Dujarric et Cie. 1906. O fr. 50.

NOTIONS FONDAMENTALES DE CHIMIE INORGANIQUE. By Ch. Moureau. Paris: Gauthier-Villars. 1906. 4+320 pp. 7 fr. 50.

L'ACTION DIASTASIQUE DANS LES FERMENTATIONS INDUSTRIELLES, CHIMIE PASTORIENNE. By E. Diederich. Paris: J. Rousset. 1906. 244 pp. 4 francs.

FABRICATION DE LA GLUCOSE, DE LA DEXTRINE, DE L'AMIDON. By J. Fritsch. Paris: J. Rousset. 1906. 224 pp. 6 francs.

POTABLE WATER AND METHODS OF DETECTING IMPURITIES. By Moses Nelson Baker. Second Edition. New York: D. Van Nostrand Co. 1906. 3+105 pp. $0.50.

COMPLETE COURSE IN CANNING: BEING A THOROUGH EXPOSITION OF THE BEST PRACTICAL METHODS OF HERMETICALLY SEALING CANNED GOODS, AND PRESERVING FRUITS AND VEGETABLES, BY AN EXPERT PROCESSOR AND CHEMIST. Baltimore: Trade Co. 1906. 182 pp. $5.00.

THE CHEMICAL ANALYSIS OF IRON: A COMPLETE ACCOUNT OF ALL THE BEST KNOWN METHODS FOR THE ANALYSIS OF IRON, STEEL, PIG-IRON, IRON ORE... Sixth Edition. By Andrew Alexander Blair. Philadelphia: Lippincott Co. 1906. 11+328 pp. $4.00.

GASOLINE ENGINE IGNITION. By E. Joseph Williams. Cincinnati: Gas Engine Publishing Co. 1906. 3+92+2 pp. $1.00.

THE PRINCIPLES OF QUALITATIVE ANALYSIS FROM THE STANDPOINT OF THE THEORY OF ELECTROLYTIC DISSOCIATION AND THE LAW OF MASS ACTION. By Wilhelm Carl Böttger. Translated by W. Gabb Smeaton. Philadelphia: P. Blakiston's Son & Co. 1906. 16+300 pp. $2.00.